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THE INSTITUTE OF PETROLEUM

AN Ordinary General Meeting of the Institute of Petroleum was held at 61 New Cavendish Street, London, W.1, on 15 March 1961, the Chair being taken by Julian M. Leonard, President of the Institute.

The General Secretary read the minutes of the previous meeting, which were confirmed and signed as a correct record.

The President introduced the authors, and the following paper was then presented in summary by Mr Groszek.

SURFACE-ACTIVE COMPOUNDS IN LUBRICATING OILS *

By A. J. GROSZEK † (Associate Fellow) and D. J. PALMER †

INTRODUCTION

MINERAL lubricating oils consist essentially of hydrocarbons, sulphur-containing compounds, and other compounds which contain either oxygen or both oxygen and sulphur. The latter compounds can exhibit surface activity similar to many other compounds in which functional groups, such as hydroxyl and carbonyl, are attached to relatively non-polar hydrocarbon radicals.

It has been known for some time that mineral oils, both prior to and after refining, contain resins which are acidic in nature and show some surface activity. These resins contain a substantial proportion of oxygen, and generally their proportion in the oils increases on oxidation.[1]

Previously Brook *et al* [2] have shown that materials similar to resins can be isolated from lubricating oils by selective adsorption on magnesium oxide. A small proportion of the oil becomes very strongly attached to the adsorbent and can be liberated only by dissolving the latter in mineral acids. Such compounds have been found to be strongly surface-active.

A review of recent publications in the literature concerning the effect of surface-active compounds on the properties of lubricating oils indicates that such compounds can affect their performance in practice in three main respects. These are: (*a*) reduction of wear;[3-12] (*b*) dispersion of sludge and lacquer-forming constituents;[2, 13, 14] and (*c*) lacquer formation.[2, 15-19] From this it is clear that surface-active compounds can play an important role in lubricating oil quality.

The present paper describes work designed to elucidate the effect that the surface-active materials may have on the quality of lubricating oils containing them, and to learn more about their nature. To this effect, various lubricating oils have been examined with respect to the amounts of surface-active material they contain and the ease of formation of such materials on oxidation.

To examine the effect of the nature of lubricating oils on the type of surface-active material formed on oxidation, different oil fractions have been oxidized and the surface-active materials formed isolated and examined.

EXPERIMENTAL

The lubricating oils used in the major part of this investigation were two blended SAE 50 oils of high viscosity index (oils A and B) and two solvent refined residual bright stocks, also of high viscosity index (oils I and J).

In addition, a restricted amount of work was carried out on six blended SAE 50 oils, similar to A and B, but derived from different crudes. These oils are referred to as oils C, D, etc., to H. Analytical data for oils A, B, I, and J are given in Table I.

TABLE I

Analytical Data for Oils A, B, I, and J

Property \ Oil	A	B	I	J
Specific gravity at 60° F	0·885	0·896	0·905	0·894
Kinematic viscosity at 100° F, cS	263·6	265·4	546·7	550·1
Kinematic viscosity at 210° F, cS	20·03	20·31	32·51	32·62
Viscosity index	95	96	97	97
Acidity, mg KOH/g	<0·05	0·02	—	<0·05
Saponification value, mg KOH/g	None	0·1	—	—
Ramsbottom carbon residue, % wt	0·34	0·26	0·46	0·29
Sulphur content, % wt	0·24	1·38	1·51	0·60
IP 48 Oxidation Test:				
Kinematic viscosity at 100° F after oxidation, cS	349·2	379·2	702·1	629·3
Viscosity ratio	1·32	1·42	1·28	1·15
Ramsbottom carbon residue after oxidation, % wt	0·83	1·00	1·04	0·60
Carbon residue increase, % wt	0·49	0·74	0·58	0·31

Oils A and B are blended oils of SAE 50 grade. Oils I and J are residual bright stocks.

The work carried out can be conveniently divided into the following categories:

1. The isolation and estimation of the surface-active materials present in the oils both before and after periods of oxidation, and also in certain fractions derived from the oils, after these fractions had been submitted to similar periods of oxidation.

* MS received 15 August 1960. † The British Petroleum Co. Ltd, BP Research Centre, Sunbury-on-Thames, Middlesex.

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* MS received 15 August 1960. † The British Petroleum Co. Ltd, BP Research Centre, Sunbury-on-Thames, Middlesex.

K K

2. The study of the surface-active materials so obtained by

(*a*) Infra-red spectroscopic, chromatographic, and general analysis.

(*b*) Construction of pressure/area isotherms for monomolecular layers on aqueous substrates using the hydrophile balance.

(*c*) Carbon sedimentation tests.

(*d*) Wear prevention tests using the four-ball machine.

Isolation and Estimation of Surface-Active Materials

To isolate and determine the surface-active material in an oil, the following chromatographic separation on magnesium oxide was employed.

10 g of the oil, dissolved in *n*-heptane, were adsorbed on to 40 g of heavy magnesium oxide contained in a chromatographic column 40 cm long and 2 cm id, the oxide having previously been wetted with *n*-heptane. After adsorption, the oil was first exhaustively eluted with *n*-heptane (the eluted material being referred to as the heptane eluate and constituting about 96–97 per cent of the oil), and then with benzene and acetone (benzene/acetone eluate constituting about 2 per cent of the oil). Finally, the dark-coloured surface-active material retained by the magnesium oxide was recovered by dissolving the latter in hydrochloric acid and extracting the liberated material with 40/60 petroleum ether.

In order to determine the effect of oxidation on the contents of surface-active material in the oils, as determined by the above method, the oils were oxidized by heating in open beakers in the presence of air for 60-hour periods at either 120° or 200° C. 25-ml portions of the oils were oxidized using 100-ml tall form beakers.

TABLE II

Effect of Temperature of Oxidation on Formation of Surface-Active Material (Time of Oxidation—60 Hours)

Oil	Surface-active material, % wt			% C_A in aromatic fraction of oil
	Un-oxidized oil	Oil oxidized at 120° C	Oil oxidized at 200° C	
A	0·6	1·0	4·6	21·6
B	0·45	0·4	2·4	12·6
C	0·1	0·2	3·8	14·5
D	0·25	0·5	4·8	26·0
E	0·4	0·65	4·65	23·2
F	0·65	1·1	4·95	21·4
G	0·5	1·2	—	—
H	0·25	1·0	—	—

The contents of surface-active material in the various oils, both before and after oxidation, are given in Table II.

Similar oxidation and extraction experiments were also carried out on fractions of varying chemical type separated from the oils. The fractions were obtained by a chromatographic separation carried out on silica gel as given below, the method dividing the oil into a saturate portion, containing the paraffins and naphthenes and referred to as fraction 1, and one or more aromatic fractions (fractions 2, 3, etc). The latter fractions contain, in addition to aromatic hydrocarbons, sulphur, oxygen, and any nitrogen-containing compounds.

To carry out the separation, a sample of oil (5 g) was dissolved in 3 ml *n*-heptane and 2 ml benzene and adsorbed on to 100–200-mesh silica gel contained in a chromatographic column 120 cm long and 1·5 cm id, expanding to 3·5 cm for the top 10 cm. The silica gel, which was previously wetted with *n*-heptane, was contained to a depth of 115 cm in the column.

After adsorption, fractions 1, 2, and 3 were eluted from the column with *n*-heptane. The heptane was allowed to flow through the column at approximately 20 ml/hr, 10-ml portions being collected in a revolving fraction collector set to change receivers at 30-minute intervals. The cuts between the fractions were made by the usual methods involving the measurement of refractive indexes, ultra-violet fluorescence tests, and the trial evaporation of test portions of eluate. The most strongly adsorbed fraction (fraction 4) was recovered by elution with either chloroform/alcohol or *iso*propyl/ethyl alcohol mixtures. In later experiments a larger column was used in order to increase the amounts of the various fractions obtained. The dimensions of this column were: length 150 cm, id 4 cm, widening to 7 cm over the top 15 cm, and the amount of the oil charged to the column was 60 g. As previously, the first three fractions were eluted with *n*-heptane and the final fraction with ethyl and *iso*propyl alcohols.

TABLE III

Fractions Separated by Chromatography on Silica Gel

Oil	Fraction	% wt of total oil	Sulphur, % wt	Refractive index n_D^{20}	Surface-active material produced by oxidation of fraction at 120° C for 60 hours, % wt
A	Saturates	69·0	0·05	1·4759	1·1
	Aromatics	31·0	0·34	1·5023	3·1
B	Saturates	60·0	0·1	1·4789	1·2
	Aromatics	40·0	2·74	1·5047	2·6
I	Saturates (1)	69·5	—	1·4860	0·5
	Aromatics (2)	7·3	—	1·5136	1·4
	Aromatics (3)	10·4	4·2	1·5144	1·2
	Aromatics (4)	9·6	5·3	1·5140	17·4
J	Saturates (1)	64·5	—	1·4828	0·3
	Aromatics (2)	18·9	—	1·4960	0·7
	Aromatics (3)	6·5	2·6	1·5120	0·7
	Aromatics (4)	4·7	3·9	1·5166	15·2

Table III lists the relative proportions of the various fractions so obtained, together with some relevant analytical data and the amounts of surface-active

material produced by the fractions after oxidation at 120° C. It will be noted that only two fractions are listed for oils A and B, a saturate and an aromatic fraction. These were obtained by the elution of the saturate portion (fraction 1) with *n*-heptane and the remainder of the oil with *iso*propyl alcohol (fraction 2).

Properties of Surface-Active Materials

(*a*) *Infra-red Spectra, Chromatographic and Analytical Data.* Analytical data for two typical surface-active materials isolated during this work (from oils A and B) are given in Table IV. Infra-red absorption spectra of the fractions obtained from oils A and B by the chromatographic method using magnesium oxide are presented in Figs 1 and 2.

TABLE IV

Analytical Data for Surface-Active Materials Separated from Oils A and B

Surface-active material from oil	A	B
Molecular weight	995	970
Ash, % wt	1·3	2·0
Acidity, mg KOH/g	39	28
Saponification value, mg KOH/g	82	38
Hydroxyl groups, % wt	0·9	1·4
Carbon content, % wt	80·4	81·02
Hydrogen content, % wt	12·2	11·42
Sulphur content, % wt	0·20	2·1
Nitrogen content, % wt	0·19	—

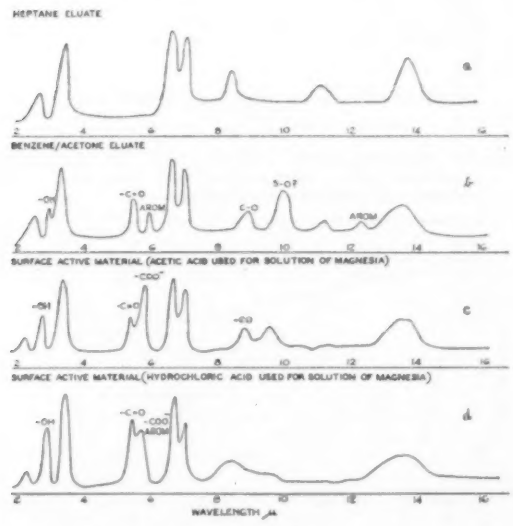
HEPTANE ELUATE
BENZENE/ACETONE ELUATE
SURFACE ACTIVE MATERIAL (ACETIC ACID USED FOR SOLUTION OF MAGNESIA)
SURFACE ACTIVE MATERIAL (HYDROCHLORIC ACID USED FOR SOLUTION OF MAGNESIA)
WAVELENGTH, μ

FIG 1

INFRA-RED ABSORPTION SPECTRA FOR FRACTIONS SEPARATED FROM OIL A BY CHROMATOGRAPHY ON MAGNESIUM OXIDE

Table V gives the results of a separation of the surface-active material from oil A using a chromatographic method involving selective adsorption on silica gel. The material was adsorbed on to silica gel in a small chromatographic column, and then eluted successively with pentane, benzene, alcohol, and pyridine. The table gives, in addition to the proportions of the material eluted, the extinction coefficients for carbonyl absorption, as determined by infra-red spectroscopy.

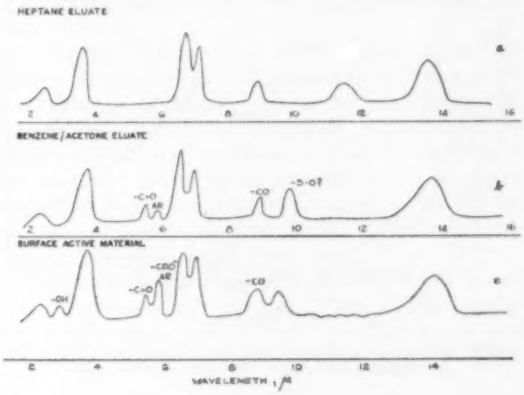

FIG 2

INFRA-RED ABSORPTION SPECTRA FOR FRACTIONS SEPARATED FROM OIL B BY CHROMATOGRAPHY ON MAGNESIUM OXIDE

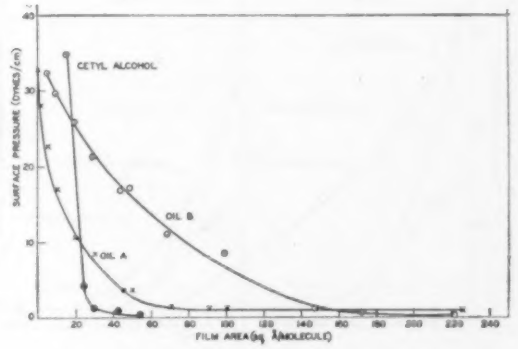

FIG 3

PRESSURE/AREA ISOTHERMS FOR TYPICAL SURFACE-ACTIVE MATERIALS FROM LUBRICATING OILS COMPARED WITH CETYL ALCOHOL

TABLE V

Fractions of Surface-Active Material from Oil A

Eluent	Oil eluted, % wt	Extinction coefficients for $C=O$ absorption bands
n-Pentane	52·5	0·077
Benzene	24·8	0·083
Ethyl alcohol	15·8	0·265
Pyridine	6·9	0·132

(*b*) *Properties of Unimolecular Films on Water.*

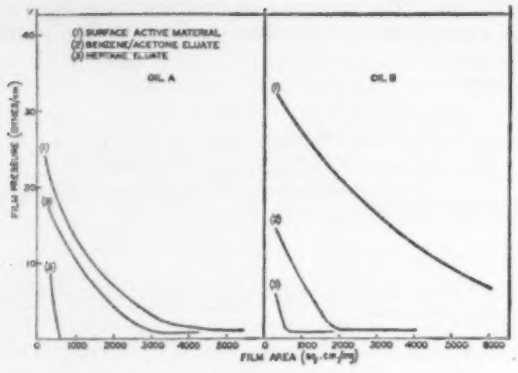

FIG 4

PRESSURE/AREA ISOTHERMS FOR OIL FRACTIONS SEPARATED BY CHROMATOGRAPHY ON MAGNESIUM OXIDE

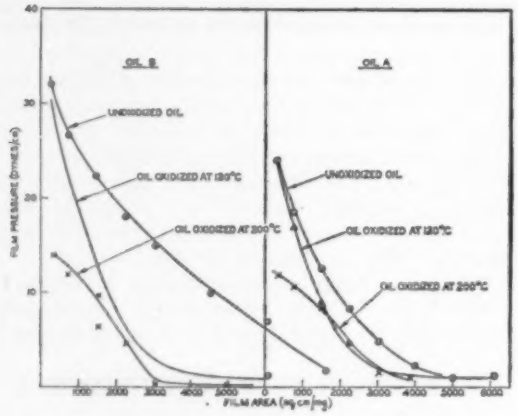

FIG 5

PRESSURE/AREA ISOTHERMS FOR SURFACE-ACTIVE MATERIALS PRODUCED BY OXIDATION OF OILS A AND B

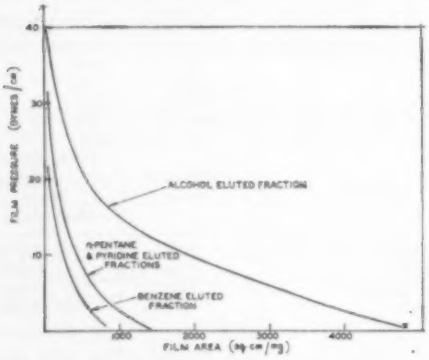

FIG 6

PRESSURE/AREA ISOTHERMS FOR FRACTIONS OF SURFACE-ACTIVE MATERIAL FROM OIL A

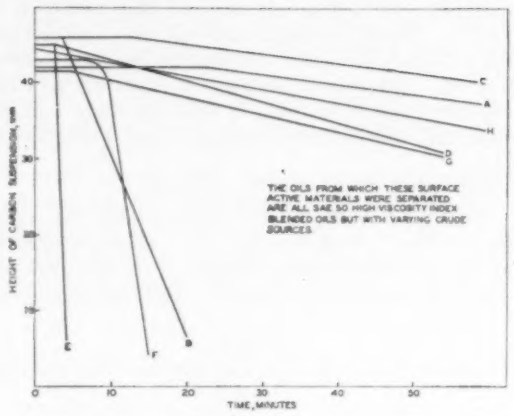
THE OILS FROM WHICH THESE SURFACE ACTIVE MATERIALS WERE SEPARATED ARE ALL SAE 50 HIGH VISCOSITY INDEX BLENDED OILS BUT WITH VARYING CRUDE SOURCES.
HEIGHT OF CARBON SUSPENSION, mm
TIME, MINUTES

FIG 7

CARBON SEDIMENTATION CURVES FOR SURFACE-ACTIVE MATERIALS SEPARATED FROM OILS OF VARIOUS ORIGIN

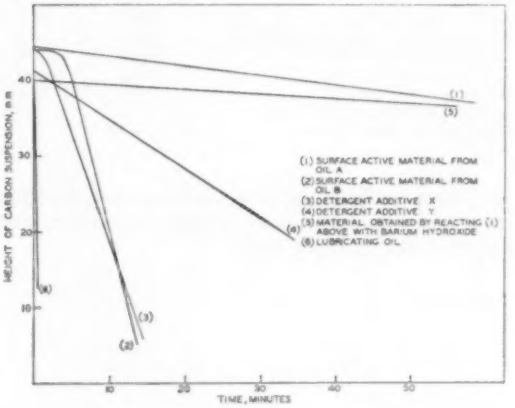
(1) SURFACE ACTIVE MATERIAL FROM OIL A
(2) SURFACE ACTIVE MATERIAL FROM OIL B
(3) DETERGENT ADDITIVE X
(4) DETERGENT ADDITIVE Y
(5) MATERIAL OBTAINED BY REACTING (1) ABOVE WITH BARIUM HYDROXIDE
(6) LUBRICATING OIL
HEIGHT OF CARBON SUSPENSION, mm
TIME, MINUTES

FIG 8

CARBON SEDIMENTATION CURVES FOR SURFACE-ACTIVE MATERIALS FROM LUBRICATING OILS COMPARED WITH COMMERCIAL DETERGENT ADDITIVES

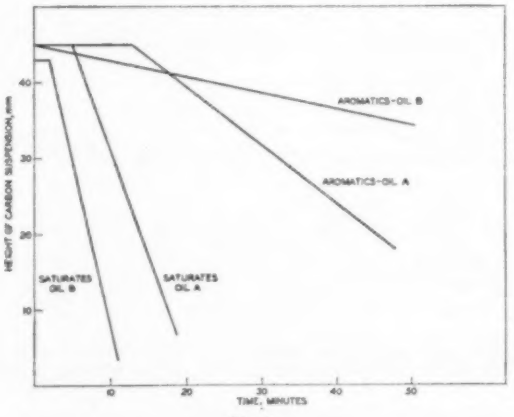

FIG 9

CARBON SEDIMENTATION CURVES FOR SURFACE-ACTIVE MATERIALS PRODUCED BY OXIDATION OF FRACTIONS FROM OILS A AND B

Pressure/area isotherms for unimolecular films of the various surface-active materials were determined by the usual procedure[20] involving the use of a film balance. The film areas are here expressed as area

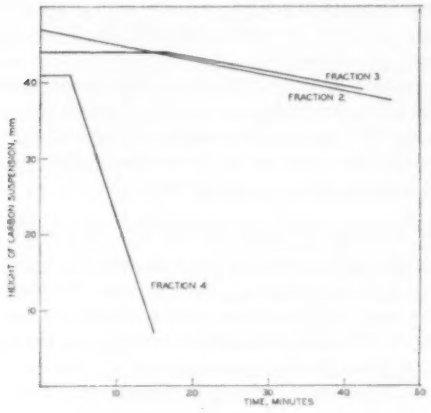

FIG 10

CARBON SEDIMENTATION CURVES FOR SURFACE-ACTIVE MATERIALS PRODUCED BY OXIDATION OF FRACTIONS FROM OIL I

per mg of material examined or, where molecular weights are available, as area per molecule. In Fig 3 the isotherms of the surface-active materials are compared with that of cetyl alcohol, and in Fig 4 with

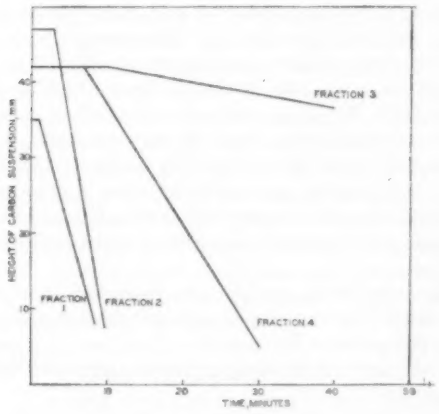

FIG 11

CARBON SEDIMENTATION CURVES FOR SURFACE-ACTIVE MATERIALS PRODUCED BY OXIDATION OF FRACTIONS FROM OIL J

those of the other fractions produced by chromatography on magnesium oxide. Fig 5 gives the isotherms for surface-active materials separated from oils after oxidation at various temperatures, and Fig 6 the isotherms for the fractions of surface-active material from oil A.

All the isotherms were determined at room temperature (*ca* 20° C).

(*c*) *Carbon Sedimentation Tests.* These tests were carried out to evaluate the dispersant qualities of the surface-active materials, and to compare them with commercially available detergent additives. Two additives were used (referred to here as Additive X and Additive Y), both in current use as detergent motor oil additives. Additive X is of the metal phenate/sulphonate type, Additive Y the metal sulphonate/thiophosphate type.

The procedure used was to vigorously shake 2·5 ml of a 0·5 per cent w/v solution of the material under test with 25 mg of carbon black * in a 3-inch × $\frac{3}{8}$-inch

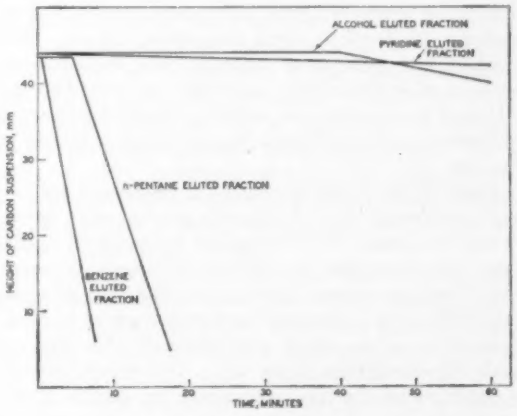

FIG 12

CARBON SEDIMENTATION CURVES FOR FRACTIONS OF SURFACE-ACTIVE MATERIAL FROM OIL A

flat bottom glass tube, and to follow the rate of sedimentation of the black, on standing, by measuring the height of suspended material after various time intervals. All the tests were carried out at room temperature using *n*-heptane as a solvent. The results so obtained are graphed in Figs 7–12 inclusive.

(*d*) *Wear Tests.* The wear-preventive properties of some of the surface-active materials obtained were studied using the four-ball machine. This machine is generally used for the study of seizure resistance of EP lubricants, and its method of use is fully described.[21] For this application, however, the machine was run for one hour at a constant loading of 15 kg, the balls being lubricated by solutions of the material under test in white paraffin. No seizure occurred, and the wear was determined by measuring the mean

* Philblack G, a furnace black, marketed by R. W. Greef and Co. Ltd, London.

diameter of the wear spots on the lower three balls. The results obtained are given in Table VI.

TABLE VI

Material	Mean wear spot diameter, mm
Medicinal paraffin	0·748
Medicinal paraffin containing:	
(*a*) 2% surface-active material from oil A	0·621
(*b*) 2% surface-active material from oil A neutralized with barium hydroxide	0·756
(*c*) 2% surface-active material from oil B	0·872

DISCUSSION

Previous work by Brook *et al*[2] has shown that materials exhibiting surface activity and the power to disperse carbon black in non-polar media can readily be separated from lubricating oils by a chromatographic method using magnesium oxide. This method has been used to study the variations in content of surface-active materials between different oils, and to examine the surface chemical properties of these materials and their formation by oxidation of the oils.

Table II shows the variations in content of surface-active material between the oils studied, and the increase in surface-active materials produced by oxidation. It is seen that the response of the oils to formation of surface-active materials on oxidation increases markedly with increasing temperature, and of particular note is the rough correlation of this response with the aromaticity of the oils. This latter quantity is represented by the percentage of carbon atoms present in aromatic structures (% C_A) in the aromatic fraction of the oil (as separated by silica gel chromatography). The % C_A was here determined by a recently developed infra-red spectroscopic method.[22]

The greater ability of the aromatic fractions to produce surface-active materials can be seen from an examination of Table III.

The appearance of the isolated surface-active materials is generally that of soft pitch. The materials produced by oxidation at the higher temperature (200° C) are, however, more solid in character. When the oxidized oils are extracted using smaller magnesium oxide to oil ratios (2 to 5 per cent by weight) the surface-active materials obtained are similar to hard asphalts. Such materials are often referred to as resins in the literature.

As will be realized, these surface-active materials are very strongly held by magnesium oxide, the adsorption complex being unbroken even by benzene and acetone. Bearing in mind the alkaline nature of the oxide, this would indicate that the surface-active materials have acidic properties, and this is confirmed by the acid values given in Table IV.

The oil fractions eluted from magnesium oxide by benzene and acetone are also surface-active to some degree and, like the strongly retained materials, have been shown by infra-red spectroscopy to contain carbonyl and, possibly, sulphoxide groups. Differences between the two fractions do, however, exist (Figs 1 and 2), and this is seen especially in their surface chemical properties.

The surface activity of these materials can be readily increased by oxidation, a period of oxidation of 60 hours at 120° C in some cases converting up to 25 per cent of the material to the surface-active material which is retained by magnesium oxide.

Chemical Structure of Surface-Active Compounds

The materials retained by magnesium oxide after elution with benzene and acetone are complex mixtures of many different types of compounds, a common feature of them all being the existence of one or more polar groups attached to a non-polar radical. The infra-red spectra of these materials are essentially those of a hydrocarbon type oil containing hydroxyl, carbonyl, and sulphoxide groups.

Two spectra are shown for the surface-active material isloated from oil A, the first referring to the material obtained by decomposing the magnesium oxide with acetic acid and the other to that using hydrochloric acid. The latter acid decomposes a larger proportion of the magnesium salts of the organic acids (Fig 1 (*c*) and 1 (*d*) respectively).

As expected, the acid values of the surface-active materials are relatively high, about 30 mg/KOH/g, which can be compared with acid values of less than unity for the original oils. The average molecular weight of the surface-active materials is of the order of 1000, or twice that of the oils from which they are extracted. The proportion of acidic molecules in the materials is therefore about 70 per cent for oil A and 50 per cent for oil B (*cf* Table IV), assuming that there is one acid group per molecule. The saponification values of the materials are higher than the acid values, indicating the presence of ester or other saponifiable groups.

The sum of the percentages of carbon, hydrogen, and sulphur in the surface-active materials are lower than 100 per cent by some 6 to 7 per cent, suggesting that the amount of oxygen in the samples is of this order.

Assuming that oxygen is evenly distributed in all the molecules of the material, this oxygen content would correspond to 4 atoms of oxygen per molecule. This indicates that the molecules of the surface-active materials contain more than one oxygen-containing group per molecule.

The infra-red spectra of the surface-active materials show the presence of metal carboxylate, carboxylic acid, and hydroxyl groups in addition to long-chain paraffinic and some aromatic groups. The main peak

characterizing the latter group is in most cases overshadowed by a strong peak characterizing the metal carboxyl group. The presence of such a group indicates that at least a part of the surface-active material is combined with a metal which is probably magnesium. This magnesium compound exhibits a surprising resistance to decomposition by strong acids, the spectra indicating that more of it is decomposed by hydrochloric acid than by acetic acid. The extraordinary stability of this compound may be due to the chelate linkages binding the metal to hydroxyl and acid groups.

The spectra for the benzene/acetone eluates from magnesium oxide are given in Figs 1 (*b*) and 2 (*b*). They are similar to spectra obtained for the alcohol eluted fractions from silica gel. There are peaks corresponding to carbonyl groups, aromatic rings, and hydroxyl groups, and relatively strong peaks at 9·8 μ, which may be due to sulphoxide groups. The latter peaks are very prominent in most of the benzene/acetone eluates, but are absent in the spectra of most of the surface-active materials. Hydroxyl groups occur only in the benzene/acetone eluates from oil A. The peak heights for the carbonyl groups in the benzene/acetone eluates from magnesium oxide are less than those in the surface-active materials, and the same applies to the peaks characterizing hydroxyl groups. There is general similarity between the spectra of the benzene/acetone eluates obtained from all the oils examined, which is surprising in view of the fact that these are derived from different sources. The significance of the assumed existence of sulphoxide groups is not fully understood at present, but it is thought that many interesting chemical properties of these fractions would be connected with such groups.

That the surface-active materials are complex mixtures is shown by their ready separation (Table V) into fractions of varying degrees of polarity. As is seen from the table, the major proportion of the carbonyl content is present in the last 20 per cent eluted from the column, this probably contributing to the increased strength of adsorption of these fractions to the gel. The increase is not consistent, however, the final fraction having only half the carbonyl content of the penultimate fraction.

Properties of Surface-Active Materials

(*a*) *Properties of Unimolecular Films.* The structure of the surface-active materials is partly elucidated by a study of the properties of their monomolecular films on the surface of water, as determined using the hydrophile balance. In Fig 3 the isotherms of films of the surface-active materials isolated from oils A and B are compared with that of cetyl alcohol. The latter material forms a condensed film in which the molecules become close packed with their polar ends in the water and their hydrocarbon "tails" standing vertically away from the water surface. Under these conditions each molecule occupies an area of *ca* 23 sq Å, as can be seen from the diagram. The area occupied per molecule by the surface-active materials is not so easily determined, due to a higher degree of compressibility of their films. An estimate can, however, be made by extrapolating the steeper portions of the curves back to zero pressure, and this gives values of 64 and 160 Å per molecule respectively for A and B.

It is thus evident that the area occupied by the molecules in the films of the surface-active materials is approximately three times greater for oil A, and seven times greater for oil B, than it is for cetyl alcohol. Two possible explanations of these greater areas are that a degree of branching exists in the hydrocarbon chain above the polar group attached to the water surface, or that the molecules are held at the surface by more than one polar group. The latter would possibly apply more to the material from oil B, and films of which exhibit the high compressibility characteristic of substances with more than one polar group per molecule. It has also been noted that the limiting areas (the areas obtained by extrapolating to zero pressure, as above) of the surface-active materials increase if the substrate is made alkaline. This behaviour is typical of films formed by acids or phenols, the end groups of which ionize on an alkaline substrate and repel one another by virtue of their ionic charges.

Of particular interest are the isotherms for the constituent fractions of surface-active material illustrated in Fig 6. As is seen, of the four fractions three are fairly condensed, with low compressibility, while the fourth is extremely compressible. The latter isotherm, that of the alcohol eluted fraction, is typical of a molecule possessing two distant polar molecules, and the high carbonyl extinction coefficient (see above) for this fraction would indicate that these are carbonyl groups. Comparison of Figs 4 and 6 shows that this fraction has the dominant effect on the isotherm for the total material at low pressures.

In Fig 4 the pressure/area isotherms are plotted for the fractions obtained by chromatography on magnesium oxide. The benzene/acetone eluates exert much more film pressure than the *n*-heptane eluates when the same amounts of the materials are compared on a given area. The highest pressures are given by the strongly surface-active materials obtained after decomposition of the magnesium oxide by acids.

The isotherms for the surface-active materials separated from oils after oxidation at various temperatures, shown in Fig 5, throw some light on the type of oxidation reactions taking place. Oxidation at 120° C obviously causes condensation of the film, this being much more pronounced in the material from oil B. It is possible that the unoxidized oil material contains a proportion of relatively non-polar material which

complexes with the polar material, leading to the formation of an expanded film. On mild oxidation this non-polar material is rendered polar, with consequent condensation of the total film. Oxidation at a higher temperature, however, leads to polymerization, with the consequential low collapse pressure shown.

(*b*) *Dispersion of Carbon Black.* Dispersion of sludge-forming and lacquer-forming constituents in lubricating oils is of major importance during their use in internal combustion engines. Consequently, the presence in the oils of materials capable of suspending sludge and lacquer constituents is essential. It has been found that some of the surface-active materials isolated from lubricating oils are good dispersants for carbon black in non-polar solvents, and a test involving the sedimentation of carbon in *n*-heptane, to which the surface-active material is added, has been used to evaluate their dispersive properties. A similar technique has been used by Brook *et al*[2] to evaluate the detergency of lubricating oil fractions.

It can be seen in Fig 8 that while the carbon black settles out rapidly from the *n*-heptane when total lubricating oil is used as the test material, the addition of the surface-active material can, in some cases, cause a marked stabilization of the suspension. That this degree of stabilization can vary from one oil to another is illustrated in Fig 7, where the sedimentation rates are plotted for surface-active materials separated from a range of blended oils. The sedimentation rates for the commercial detergent additives (Fig 8) are noteworthy in that they illustrate that these materials are quite inferior to some of the surface-active materials from the oils in their power to disperse carbon black.

Surface-active compounds isolated from different oxidized fractions from oils A and B were examined in an effort to find the type of hydrocarbon that yields on oxidation a surface-active material with the strongest dispersant action. Figs 9–11 show the results of these experiments. In all cases it can be seen that the surface-active materials produced by oxidation of the saturate fractions have poor dispersant properties. The materials produced by the aromatic fractions are, however, in some cases good dispersants. No correlation between dispersant power and the position of the aromatic fraction in the separation sequence on silica gel is obvious, and for a given oil the fraction producing the best dispersant can be found only by experiment. It is noteworthy that the dispersant power of the surface-active materials from these oxidized aromatic fractions are in some cases higher, and in others lower, than those of the materials separated from the whole oils.

The carbon sedimentation curves for the fractions obtained by silica gel chromatography of the surface-active material from oil A show that these fractions have widely varying dispersive powers. The fact that the alcohol and pyridine eluted fractions exhibit the greater dispersive powers indicates that this is connected with their increased carbonyl content. The power to disperse materials such as carbon black is also dependent on the non-polar portion of the molecule, and it might be expected that these two fractions would show similar pressure/area isotherms. It is noteworthy that the isotherms of all four fractions (Fig 6) are similar under high compression.

(*c*) *Effect of Surface-Active Compounds on Wear.* The series of experiments carried out using the four-ball machine shows the effect of the addition of these surface-active materials on the lubricating properties of white paraffin.

It can be seen in Table VI that the wear is significantly reduced by the solution containing material from oil A, whereas it is increased by the solution containing material isolated from oil B. Neutralization of the acid groups in material from oil A by interaction with barium hydroxide causes the wear to revert to the same level as that given by the liquid paraffin. This indicates that the acid groups in this material are an important factor in the reduction of wear.

CONCLUSIONS

An examination of lubricating oils from various sources has shown that they invariably contain small quantities of material which is strongly surface-active. The extent of surface activity of these materials depends on the proportions of polar groups in their molecules. The fractions of the oils showing the strongest surface-active properties possess probably more than one polar group per molecule and can be isolated from the oils by adsorption on magnesium oxide.

It has been confirmed that these surface-active materials can act as powerful dispersants for carbon black at room temperature—more powerful in fact than certain well-known commercial detergent additives. However, the activity of the various materials is not the same, and it is considered that the surface-active compounds which disperse carbon black well would probably also disperse engine sludge and lacquer-forming constituents. Consequently, it is concluded that the ability of lubricating oils to produce satisfactory surface-active compounds in sufficient concentrations during service is highly desirable.

The fact that some of the surface-active materials affected the wear of steel balls in the four-ball machine test confirms the importance of the materials in respect of wear and indicates that this effect depends on their chemical nature.

The exact chemical nature characterizing the surface-active compounds which efficiently disperse carbon black and reduce wear is not known at present, nor is the exact structure of the lubricating oil fractions which yield such satisfactory compounds on

oxidation. There are, however, indications suggesting that such compounds are derived from the aromatic hydrocarbons in the oil. It is also apparent that the most efficient carbon-dispersing materials are characterized by a relatively high content of carboxyl groups.

ACKNOWLEDGMENT

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DISCUSSION

I. R. H. Crail (Castrol Ltd): I should like to welcome the paper for two special reasons. First, because it tells us something more about what is in mineral oils, which is a very good thing, for we know really very little of their detailed structure. Secondly, because the authors have allied a number of the physico-chemical techniques to help in analysing organic chemicals. I think this is a system that will be used very much in the future. They went on to ultra-complex molecules, from the point of view of infra-red spectroscopy, and I do think this is a field that ir work is just moving into, and they are to be congratulated in allying these various techniques.

With regard to the ir work, I would like to ask them one or two questions. First of all, they thought they had got a sulphoxide peak at one stage. But I do notice that if one looks at the per cent sulphur in their compounds, the sulphoxide peak seems to go up as the sulphur goes down, and I wonder what the other sulphur is doing, and whether the authors have any thoughts on that.

Secondly, they have mentioned both carboxylic acid and hydroxyl groups, and they rather suggest that both these occur. Looking at the ir traces, it did appear that the hydroxyl groups went up at just about the same sort of rate as the carboxylic acid carbonyl group went up. I wondered whether perhaps the OH group was not due to the carboxylic acid hydroxyl group, if there had been very few around, it would be the same as in dilute solution.

I agree that from the stat value and the acid value it would appear that certain esters are present; and again, I wonder if they have managed to separate the carbonyl peaks of esters and acids. I feel that even though they are very close together, by running a difference trace in a double-beamed instrument, using two materials from A and B, they might well be able to spot the presence of the ester.

The term "dispersion" is bandied about a lot these days, and there seem to be two fields developing—traditional detergency and coal flood dispersancy. Have the authors any information about coal flood dispersancy properties of these materials, because they appear to be large molecules and poly-polar molecules. When one sees the patent literature these days one repeatedly reads about materials with poly-polar groups attached to them.

In this respect I would suggest that the carbon black dispersion test is unsatisfactory as far as coal flood dispersancy is concerned, though it may have more use in the detergency field. Speaking perhaps with the tongue in the cheek, I did wonder whether I would see them advocating the removal of anti-oxidants from oils, so that one might more easily obtain oxidized materials and have better detergents. But it seems that the graphs indicated that the degree of detergency will vary from temperature to temperature. Hence, if one selects any given oil, and uses it in various engines, one may expect varying degrees of oxidation taking place in various engines, and from driver to driver in the actual field. Therefore it would seem that one would get a very considerable difference in degree of detergency, depending on what oil, and possibly even what batch of oil, was used; and also on what engine and what driver was driving.

Would the authors agree that in this sort of situation, the best way out is to refine one's base oils more highly; to remove these materials, which not only from the point of view of detergency but also from wear characteristics apparently vary (some are pro-wear, some anti-wear). And having highly refined them, put in additional conventional additives, and hence get more closely defined, more constant, materials. In other words, use a balanced mixture of known additives, rather than what happens to be in the oil at the minute.

A. J. Groszek: Regarding the first point, the presence of sulphoxide groups. Some of the oil fractions eluted from magnesium oxide by benzene and acetone contain absorption bands at 9·8 μ; this also occurs in certain

types of synthetic sulphoxide compounds that were analysed. This led us to believe that the band at 9·8 μ might be produced by sulphoxide groups present in these materials. We cannot say really that there are any tendencies visible in the occurrence of the group. Some polar oil fractions show this group; other materials do not show any trace of it at all; we cannot really connect this with sulphur content of the oils from which the fractions are isolated, nor with any other property of the material which we have separated. We are not absolutely certain that the band at 9·8 μ corresponds to a sulphoxide group.

Secondly, the question of whether the hydroxyl absorption band is partly due to the hydroxyl present in carboxylic groups. It is quite true that there is a tendency for the hydroxyl group absorption to increase with the carbonyl absorption. However, the examination of numerous spectra of different types of the surface-active materials shows little correlation between the heights of the carbonyl absorption bands and the heights of the bands due to hydroxyl groups.

In addition, we have established the presence of OH groups by chemical analysis, using conventional chemical methods. It seems therefore that a certain amount of hydroxyl group is present in some of the surface-active materials.

On the question of dispersion and detergency. When we refer to detergent properties of the surface-active materials we have in mind their capacity to reduce lacquer formation, ring-sticking, and formation of sludge at relatively high temperatures. We have found that carbon dispersion tests used correlate with the detergent properties of the surface-active materials acting under high temperature conditions, such as those prevailing in the Petter AV1 engine, or aviation engines. We do not know whether the tests would apply to the conditions under which cold-sludging takes place.

You put the question of whether it would be advisable to eliminate anti-oxidants in mineral oils to facilitate the formation of beneficial types of oxidation products. One would have to know the nature of a mineral oil very well before one could remove anti-oxidants from it. Some types of oil contain compounds that yield beneficial products on oxidation. Other types of oil are not satisfactory in this respect. We have analysed oils possessing a high viscosity index, and in such oils the material that forms on oxidation is soluble. On the other hand, oils having low viscosity index tend to give oxidation products that are not soluble and are rather troublesome. The latter oils form sludge and lacquer very readily. If one knew that the nature of an oil is such that it will produce a beneficial type of material of oxidation, the removal of anti-oxidants from the oil may be a good thing to do.

F. T. Barcroft ("Shell" Research Ltd): I noticed in Table VI that these oxidized materials, when reblended in medicinal paraffin, have wear preventive properties. What is the extent of this, and have you compared, for example, the wear prevention by these materials with something such as oleic acid, tri-cresyl phosphate, or other well-known wear-reducing agents?

A. J. Groszek: The extent of wear reduction produced by these compounds is not so great as one gets for, say, stearic acid or oleic acid. Wear tests in the four ball machine have been carried out under 15 kg load only, and one would have to carry out further tests under a series of increasing loads to compare the compounds with other wear reducing agents. The tests under a single load do not give full information, but nevertheless show that certain wear prevention properties do exist.

W. A. Snell (Lubrizol Great Britain Ltd): Some figures are given for the effectiveness of this material in dispersion tests, and I notice that one of the last illustrations gave engine results. Could some figures be given for relative engine tests on the same detergent additives which you tested in this carbon black test?

A. J. Groszek: The results similar to those produced by oxidized oil A, the oil that showed relatively good detergency, were obtained with a blend containing 4·5 per cent by weight of commercial additive X, which was used in the carbon dispersion tests. The additive was of a phenate/sulphonate type and contained barium and calcium.

W. A. Snell: In the table of engine results your ring-stick ratings do not really compare with the ratings obtained on current additives used to produce MIL quality oil, on which you get absolutely no ringstick in a 120-hour test.

A. J. Groszek: No; the level of detergency that one gets from an oxidized oil is definitely lower than the level one would get from an MIL dosage of additive.

W. A. Snell: In that respect, then, the carbon dispersion test possibly does not give a significant assessment on the effectiveness of these materials in service.

J. R. Lodwick (British Petroleum Co. Ltd): I wonder whether the authors could give a little background to this work, in so far that there are certain aviation oils in which the use of additives are precluded. When you get lubricating oils which give quite different behaviours in engines I imagine that this technique might be quite useful in explaining or indicating why this is so. The authors may wish to comment on this.

A. J. Groszek: It seems that, in general, for an oil that does not contain any detergent additive, its tendency to produce on oxidation a beneficial type of detergent compound is highly desirable if it is to be used in an aviation engine. We have described a test which involves oxidation of an oil, determination of the amount of surface active material formed, and its carbon dispersion properties. This test gives quite a good indication of whether a given oil is suitable for use in aviation engines.

Dr M. F. Mohtadi (Birmingham University): I would like some clarification of the shape of the sedimentation curves. I should have thought that these could not be straight because the rate of sedimentation decreases with the increase in the apparent concentration and the viscosity of the system with time. Referring to Fig 7, for instance, line *E* has two instantaneous values, one at something like 5 mm height and the other one at 45 mm height, and this appears unusual.

On the question of the importance of experiments with dispersions of carbon black in liquid hydrocarbons or oils, to a very large extent the importance of such experiments depends on the reproducibility of the results, and one has to ensure more or less perfect initial state of the dispersion. A dispersion of carbon black in a non-viscous liquid, such as *n*-heptane, made by hand-shaking produces a more uniform dispersion than when the same amount of carbon black is shaken in lubricating oil with high viscosity. The two results are therefore not com-

parable. Curve 6 in Fig 8 seems to indicate that apparently the dispersion sedimented out very quickly. But it may also be taken that carbon black was not efficiently dispersed in the first place. Was the carbon black used in this work extracted with a solvent, or dried, before dispersion, because here again the adsorbed materials on the carbon black surface can have marked effect on the stability and the degree of peptization?

A. J. Groszek: First of all, regarding the shape of the carbon sedimentation curves. All the sedimentation tests were carried out with 0·5 per cent solutions of all the materials examined. The materials were dissolved in *n*-heptane, and 1 per cent by weight of carbon black was added. Carbon black was not extracted, it was a commercial material, the same material being used for all the tests. The technique which was used for initial dispersion of carbon black was the same for all the experiments, and since in all the cases 0·5 per cent solutions were examined, it was assumed that similar dispersions of carbon black were produced.

All the curves tended to be convex, and initially, after the shaking procedure, there was no visible sedimentation at all for a certain time. This is why the first portion of the curve in the figures is horizontal. Subsequently, there was a slow sedimentation rate which was followed, for poor dispersants, by a very rapid settling rate. The shape of the curves is convex, but, of course, when the sedimentation rate is slow, this convex shape is not very apparent.

D. J. Palmer: We might refer you to Garner's work on sedimentation, where he showed that with certain concentrations of carbon in dispersion, the larger carbon particles gradually form a network which entraps the smaller particles, the complete network subsequently collapsing and settling. It would follow that our induction time, during which we found there was no sedimentation at all, is the period during which this network is forming. In the particular case in question, the network, having formed, settled very quickly. This would explain the horizontal portion of the curve and the rapid fall afterwards.

Dr M. F. Mohtadi: My comment was concerned more with the end points of the curves, and how the sedimentation can be at a uniform rate as indicated by the straight lines, and not as a convex curve which you mention. And then again, particularly on Fig 7, Curve E, for instance, there has obviously been a disintegration of the sedimentation regime altogether. In other words, at the very end of the curve, at the time T1, at T1 plus epsilon, you have 4·5 mm height, and then at time *Ft* plus epsilon also you have none. That is really what I have been asking.

I should imagine most of these curves have had to flatten out and show, for instance, no sedimentation after a certain time, or very little indeed. I should also like to repeat my question about Curve 6 on Fig 8.

A. J. Groszek: Yes, as in all the other experiments we have here again 0·5 per cent solution of mineral oil in *n*-heptane. The viscosity of all the solutions was very similar and was largely that of *n*-heptane.

In the case of Curve 6 in Fig 8, the convexity of the curve would be shown on a larger diagram. Sedimentation for this oil is very rapid, and in the final stage the carbon forms a fairly close-packed layer at the bottom of the tube. The approach to this point is gradual and the curve is then concave. We have shown only approximate curves that do not show this concave part when the sedimentation is almost complete.

W. Pohl: I want to be a little critical of the paper, or of its inferences, and I shall be freer to do that in my new status of a retired old gentleman in that none of my remarks can now be attributed to the policies of my company.

I have no criticism of the facts, figures, and results of this paper, they seem to be clearly and patiently collected and presented—but when we talk today about dispersency and anti-wear, surely we are thinking mainly in terms of engine oils, and in these oils their importance is far greater than in industrial oils and in the more simple lubricating conditions of plain bearings. When one thinks in those terms, the logical inference of this paper seems to be that an oxidized non-additive oil is as good as, or nearly as good as, an additive-type oil, containing additives that have been deliberately put in to give dispersancy and anti-wear.

Now I find that contrary to experience, and I am driven to the conclusion therefore that the particular tests used are misleading, and that we are fooling ourselves. In spite of your Petter tests and your carbon sedimentation tests, real life experience, I think, does lead us to believe that additive oils in which these dispersant and anti-wear additives are put, behave considerably better than the mere oxidized non-additive oils.

The conclusions of the paper may be important for certain cases of non-additive oils under boundary conditions, although even there I do not think the detergency factor is important at all, but only the polar adsorption and oiliness factor, and maybe the anti-wear. But in real terms of dispersancy and anti-wear, in which the oil supplier and the oil user are interested, it seems to me that the properties of these resins are comparatively unimportant and of no practical significance.

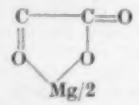
A. J. Groszek: I certainly cannot agree with Mr Pohl on this. I have mentioned the tests in which aviation engines were used demonstrating that the oils in which the right types of the surface active compounds are formed have superior performance. Also we have shown definitely that the same oils perform well in the Petter high temperature test; other oxidized oils perform very badly in these tests.

It is perhaps not surprising that the surface active compounds with relatively high oxygen and sulphur contents can have detergent properties. We have all heard a lot recently about oils containing ashless detergent additives. Such additives may not be very different in nature from some of the surface active compounds, and we know that the ashless additives are used in practice.

As I have mentioned previously, diesel engine performance of the oils containing the beneficial surface active compounds is equivalent roughly to that produced by an oil containing about 4 per cent of a phenate/sulphonate commercial additive. I think therefore that we can say definitely that improvements in detergency produced by the beneficial types of natural detergents are significant and in some cases can be very important in practice.

Dr R. W. Hay (Esso Research Ltd): Your infra-red spectra have all been done in the sodium chloride region. It might be interesting to look at the KBr region. Metal oxygen stretching vibrations occur in this area around 460 cm^{-1} (Nakamoto and Martell, *J. Phys. Chem.*, 1960, **32**, 588). You mention that the great stability of the

magnesium compounds may be due to chelate ring structures involving hydroxyl and acid groups. Carbonyl groups could also be involved in chelation, possibly producing structures of the type



Measurements in the KBr region might possibly give you an indication if this is the case.

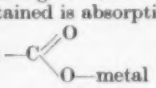
A. J. Groszek: Yes, there may be some carbonyl chelate compounds present. I am not certain actually what type of prisms were used. Perhaps Mr Jenkins can help us here.

G. I. Jenkins (BP Research Ltd): I have never actually thought of looking at these materials in the KBr region. I do not think that it would be very useful. As regards actually characterizing the type of salt that is present, work in the 6 to 7-μ region might be beneficial.

Dr R. W. Hay: If a carbonyl group is involved in chelation the frequency of the perturbed carbonyl adsorption should be shifted to lower frequencies in the sodium chloride region (Bellamy and Branch, *J. Chem. Soc.*, 1954, 4491).

G. I. Jenkins: What do you actually want to characterize?

Dr R. W. Hay: I wanted to see if the magnesium was bound in a chelate ring and not solely as a soap. You have found evidence for carboxylate ion absorption, but have none to show that chelate ring structures are involved.

G. I. Jenkins: These extracts have certainly not been examined in the KBr region, and there is no infra-red evidence to support chelate linkages. The only infra-red evidence that has been obtained is absorption in the 6 to 7-μ region, which suggests  linkages.

A. J. Groszek: We think that chelate compounds are present in the surface active materials because of the extraordinary resistance of the metal soaps to decomposition by strong mineral acids. The soaps are partially decomposed when their solutions are passed through an ion exchanger (Zeocarb 225), but even the ion exchanger does not remove all the metal from the surface active compounds. This indicates that there is an extraordinarily strong bond between some of the components of that material and the metal atoms such as magnesium. This is one of the most interesting properties of the surface active material that forms in mineral oils on oxidation, and it may well be responsible for the formation of strongly adsorbed wear-reducing films on metal surfaces.

The meeting then closed with a hearty vote of thanks to the authors.

ERRATA

It is regretted that an error in presentation appears in Tables III and V, p. 192, of the June issue of the *Journal of the Institute of Petroleum*. In columns 2 and 3 of each table the expression in the square bracket above each column applies only to the column in question. The two products are not multiplied, as is suggested by the actual heading.

In the second line of the paragraph immediately following Table III, p. 192, the word "falling" should read "rising."

VISCOSITY–TEMPERATURE EQUATIONS FOR LUBRICANTS *

By R. F. CROUCH † and A. CAMERON †

SUMMARY

A number of viscosity–temperature relationships are studied using the observation made by Duff that the subtangent of viscosity, namely, $\frac{1}{\eta}\frac{d\eta}{dt}$, is usually a polynomial in temperature. It is found that the most accurate is the Vogel formula $\eta = k \exp[b/(t+\theta)]$, a three-constant equation, which is also convenient to handle mathematically. The relatively new and rather complex formula due to Umstätter; arc sinh $\left(\log_e \frac{\eta}{\eta_o}\right) = d - n \log_e T$ appears to be as accurate as the more usual ASTM formula. Both of these are two constant equations, thereby lacking flexibility, and failing, when applied over a wide viscosity range.

INTRODUCTION

THERE have been a considerable number of viscosity–temperature laws proposed for lubricating oils since the publication of the work by Reynolds [1] on olive oil, but no study has been made of their applicability to modern products and of their comparative accuracy. This is the subject of this paper.

The work has been facilitated by an observation of Duff [2] that almost all formulæ relating temperature and viscosity can be shown to be solutions of the same type of differential equation. This is

$$-\frac{1}{\eta}\frac{d\eta}{dt} = \frac{1}{P(t)}$$

where $P(t)$ is a polynomial in t, the temperature. Many equations have been advanced to describe the variation of viscosity with temperature, there being a good bibliography of early work in a book by Hatschek,[3] but only a few are important for general use.

TABLE I

Eqn no.	Law	Subtangent $\frac{1}{\eta}\frac{d\eta}{dt}$	Author
1	$\eta = Re^{-\alpha t}$	$-\alpha$	Reynolds [1]
2	$\eta = \frac{S}{(a+t)^m}$	$-\frac{m}{(a+t)}$	Slotte [4]
3	$\eta = K \exp\left(\frac{b}{t+\theta}\right)$	$-\frac{b}{(t+\theta)^2}$	Vogel [5]
4	$\eta = C \exp\left(A + \frac{B}{T}\right)^8$	$-\frac{2B}{T}\left(A + \frac{B}{T}\right)$	Ranaiye [6]
5	$\eta + \gamma = \beta D^{1/T^c}$	$-\frac{c \log D}{T^{c+1}}\left(1 + \frac{\gamma}{\eta}\right)$	Walther–ASTM [7]
6	arc sinh $\left(\log_e \frac{\eta}{\eta_o}\right) = d - n \log_e T$ $(\eta_o = 1)$	$-\frac{n}{T}\cosh(d - n \log_e T)$	Umstätter [8]
7	$\eta = K' \exp\frac{b'}{(t+\theta')^2}$	$-\frac{2b'}{(t+\theta)^3}$	This paper

t, ° C.
T, ° Abs.
η, viscosity.
α, a, A, β, b, b', B, c, C, γ, d, D, K, K', m, n, R, S, θ, θ', constants.

In Table I these formulæ are tabulated together with their subtangents $\frac{1}{\eta}\frac{d\eta}{dt}$ and a reference to an original paper. In some cases the law was proposed by several authors. This is the case in laws 1 and 2, and reference may be made to Hatschek for further details.

These equations can be either in absolute or kinematic viscosities. In this paper all diagrams display viscosity in centistokes.

It may be noticed that Reynolds' equation is a limiting case of Vogel's equation, when the range of temperature is small where R equals $Ke^{b/\theta}$ and α is b/θ.

It was pointed out by Cameron [9] in 1945 that for many conventional oils over the range 0° to 100° C the θ in Vogel's formula could be replaced by 95 if t was in ° C. This was further studied by Rost,[10] who showed that this modification was as satisfactory as the more commonly used Walther–ASTM equation, No. 5 in the table. This was an effort to simplify the equation to a two-constant relation similar to the Walther–ASTM formula, where γ is a constant with a value of about 0·6, or the formula due to Umstätter, where η_o is set equal to 1 centistoke. Unfortunately the oils of high viscosity index do not obey these simplified formulæ, the multigrade, polymer-loaded oils in particular giving a very poor correlation over the wide temperature ranges demanded by modern requirements. It becomes evident that a three-constant equation has a better chance of success under such extreme conditions.

METHOD OF COMPARISON

In order to compare the various laws, the viscosities of two oils of −60 VI and 102 VI were determined very accurately at intervals of 5° C between −10° and 95° C. The results are listed in the appendix, together with brief details of the experimental method. Also the viscosities of a large number of oils and other fluids

* MS received 13 March 1961.

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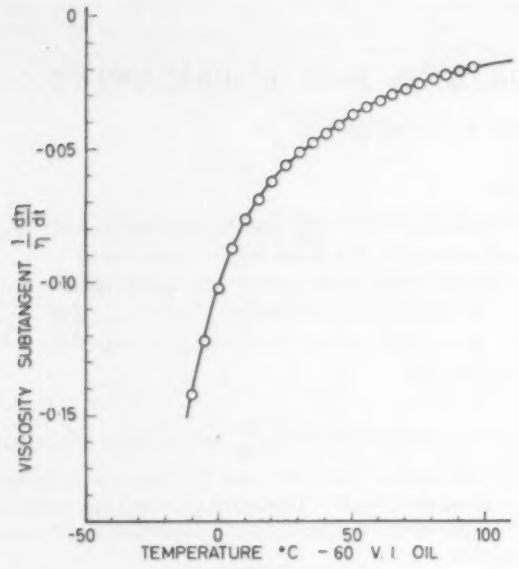

Fig 1

VISCOSITY SUBTANGENT OF −60 VI OIL CORRELATED BY VOGEL'S EQUATION

published in the literature[11] were analysed, these being normally given at fairly widely spaced temperatures, usually −53·9° C (−65° F), −40° C (−40° F), 0° C (32° F), 37·8° C (100° F), 98·9° C (210° F), 148·9° C (300° F), 204·4° C (400° F), 218·3° C (425° F), 315·6° C (600° F), 371·1° C (700° F).

The data of the −60 and the 102 VI oils were analysed by differentiating numerically the logarithm

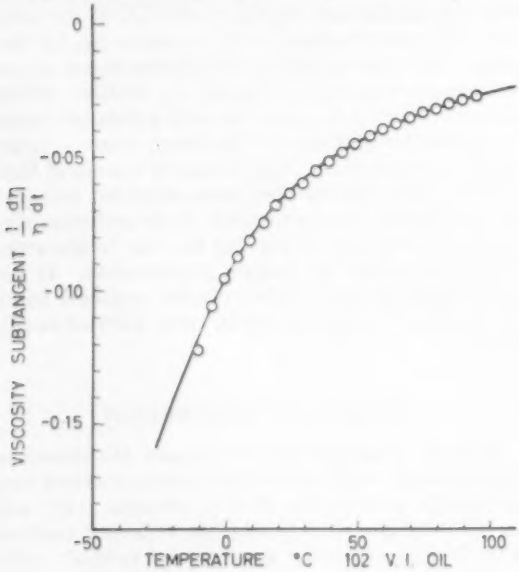

Fig 2

VISCOSITY SUBTANGENT OF 102 VI OIL CORRELATED BY VOGEL'S EQUATION

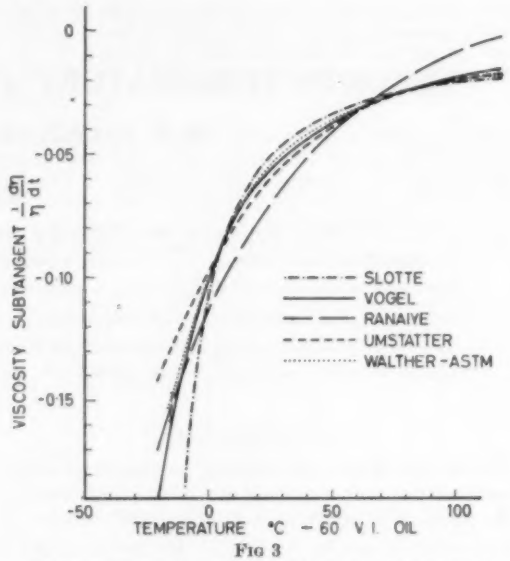

Fig 3

VISCOSITY SUBTANGENT OF −60 VI OIL CORRELATED BY VARIOUS EQUATIONS

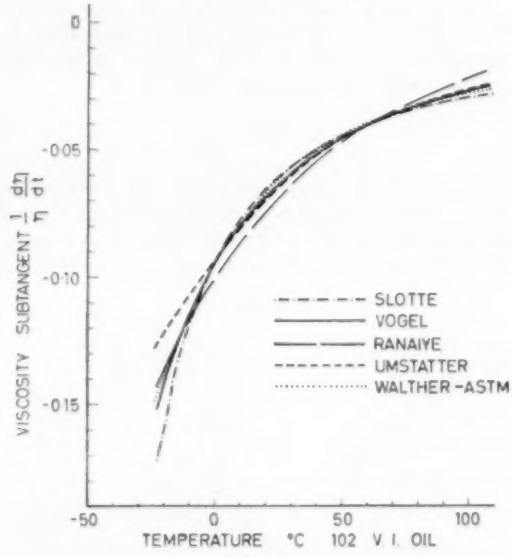

Fig 4

VISCOSITY SUBTANGENT OF 102 VI CORRELATED BY VARIOUS EQUATIONS

of the viscosity ($\log_e \eta_i$) with respect to the temperature, t, using the six-point formula of Bickley.[12] As $\frac{d(\log_e \eta_i)}{dt} = \frac{1}{\eta_i}\frac{d\eta_i}{dt}$, this gives the subtangent directly. The degree with which the subtangent determined from these measurements fits the various empirical laws is shown in Figs 1–4.

The full line in Figs 1 and 2 is given by the subtangent of the Vogel equation with appropriate values of b and θ, and the two figures show that these full

lines fit the observed points to within the experimental error. The other laws which were considered did not give as good an agreement with the experimental results as the Vogel law, and they are displayed in Figs 3 and 4. In both these figures the full line is Vogel's law taken from Figs 1 and 2, and the various dotted and broken lines represent the laws due to Slotte, Ranaiye, Walther–ASTM, and Umstätter. Reynolds' law just gives a straight line, which is not shown. Of the two-constant laws, the one due to Umstätter is the best, though it deviates somewhat at either end. This and the Walther–ASTM formula are studied in more detail later.

THE VOGEL FORMULA

The Vogel formula is a three-constant formula

$$\eta_t = K \exp\left(\frac{b}{t + \theta}\right)$$

and each constant has a definite significance.

As the exponential term is dimensionless, K gives the " thickness " of the oil, so it has the units of viscosity. This is convenient, as K is not altered by the choice of the temperature scale, and, furthermore, any change in the units of viscosity demands an equal change in K only.

The exponential parameter b has units of temperature and expresses the inherent viscosity–temperature variation of the oil. This has been used by Rost [10] and Cameron [13] to construct an index of viscosity. They showed that, for all oils, to a *first* approximation b was proportional to the logarithm of the viscosity measured at a given temperature. For a second approximation the VI of the oil must be considered.[13]

Finally, the constant θ expresses the temperature at which the oil has infinite viscosity, since when θ equals $-t$, $\exp \frac{b}{t + \theta}$ becomes infinite.

If a chart similar in purpose to the ASTM chart is to be constructed, this formula must be reduced to a two-constant law by expressing one constant in terms of the other, or putting it equal to a known value. In the earlier reference [9] this was done by putting $\theta = 95$. The attempts to find some such correlation are described in the following section.

Attempted Correlation of Vogel's Constants

The published viscosity data [11] were analysed fully to obtain values of the three constants for many liquids over a wide viscosity index range using a graphical method described later. The majority of values of θ were between 85 and 135, those for b were between 600 and 1100, and those for K between 1 and 1000. The attempts to find a correlation between θ, b and K, or η are shown in Figs 5–7.

It appears from these graphs that there is no satisfactory correlation, which, in view of the quite separate significance of the three constants, is not altogether surprising. There is, of course, a general

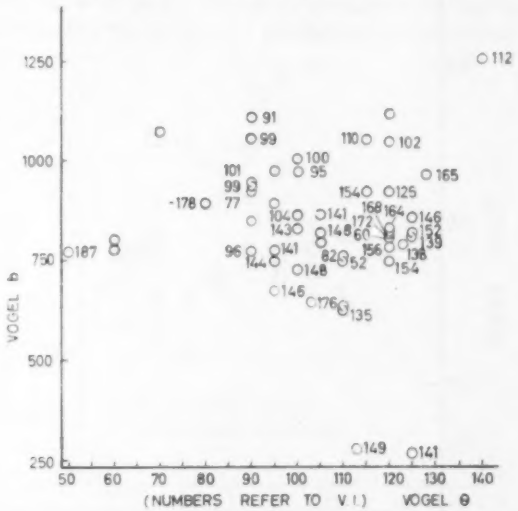

FIG 5

ATTEMPTED CORRELATION BETWEEN VOGEL'S b AND θ

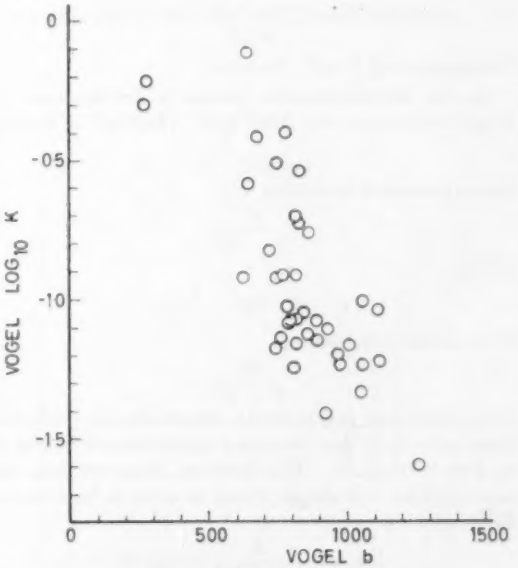

FIG 6

ATTEMPTED CORRELATION BETWEEN VOGEL'S b AND LOG K

trend relating the " thickness," K, and the viscosity–temperature parameter, b, as was pointed out in references 10 and 13. This is not precise enough to be useful and does not give any assistance in determining θ.

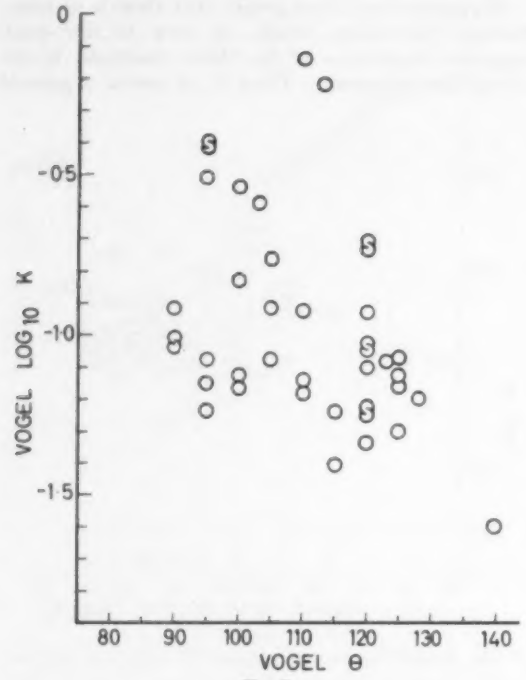

FIG 7

ATTEMPTED CORRELATION BETWEEN VOGEL'S θ AND LOG K

Development of Vogel's Equation

As no correlation was found, a development of Vogel's equation was tried next. Instead of writing

$$\eta_i = Ke^{\frac{b}{t+\theta}}$$

the exponential is written

$$\frac{b'}{(t+\theta')^2}$$

giving

$$\eta_i = K' \exp \frac{b'}{(t+\theta')^2}$$

The subtangent becomes

$$\frac{2b'}{(t+\theta')^3}$$

It appears that this formula, which fits the published data quite well, does permit a correlation of b' and θ', as Figs 8–10 show. This does not, however, help the construction of a simple chart, as even in its simplest form, namely

$$\log_e \eta_i = \frac{b}{(t+\theta')^2} + \log_e K'$$

the formula still presents axes, one of which contains the main variable t linked to a constant θ', whose value depends on the liquid considered. The correlation is, however, included for completeness.

Use of Three-constant Vogel Law

Clearly the Vogel equation, besides being accurate over a large range of products for wide ranges of

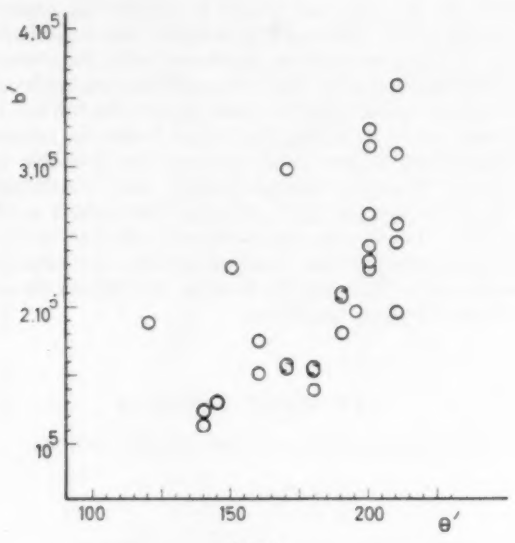

FIG 8

ATTEMPTED CORRELATION BETWEEN MODIFIED VOGEL b' AND θ

viscosity and temperature, is also easy to handle mathematically. For computing or drawing a viscosity–temperature line, the various constants have to

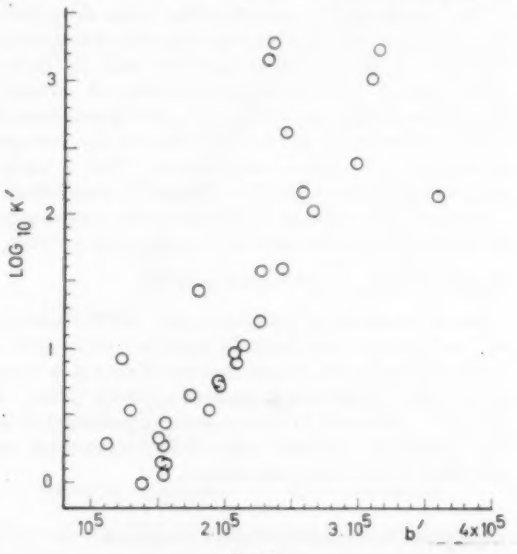

FIG 9

ATTEMPTED CORRELATION BETWEEN MODIFIED VOGEL b' AND LOG K'

be found and for this the viscosity has to be known at three temperatures.

If, however, the object is merely to draw a straight line a somewhat simpler procedure can be used. Viscosities are usually obtained at a number of standard

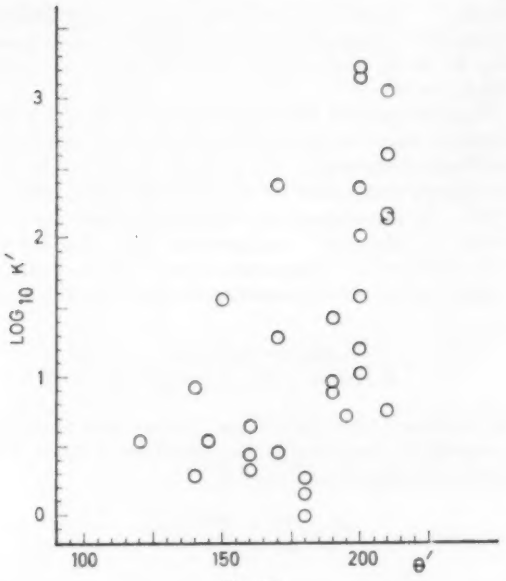

Fig 10

ATTEMPTED CORRELATION BETWEEN MODIFIED VOGEL θ AND LOG K'

temperatures, such as −53·9° C, −40° C, 0° C, 37·8° C, 98·9° C. The value of the temperature correction term θ can be anything between about 50 and 150. Therefore the axes of the graph must be a logarithmic ordinate and a reciprocal abscissa containing the constant θ, namely, $\log_e \eta$ and $1/(t + \theta)$.

The use of this graph is shown in Fig 11. Vertical lines are drawn corresponding to temperatures of 0° C, 37·8° C, 98·9° C, 148·9° C, and 218° C for values of θ = 100, 90, 80, 70, 60. Horizontal lines are drawn

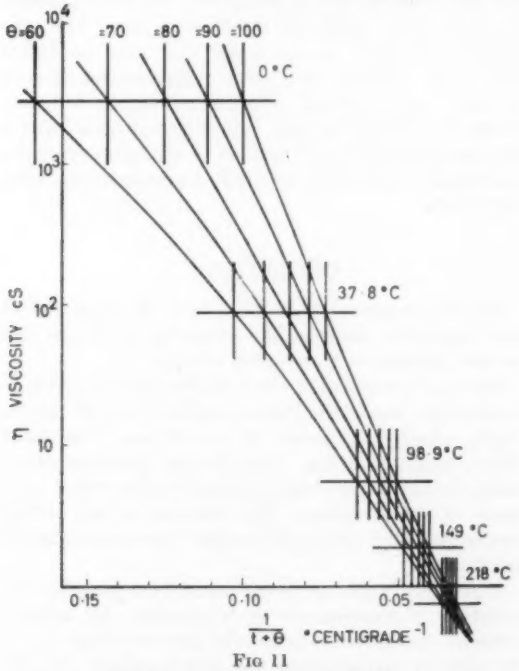

Fig 11

FLUOROLUBE STANDARD PLOTTED USING VALUES OF θ BETWEEN 60 AND 100. METHOD OF DETERMINING θ

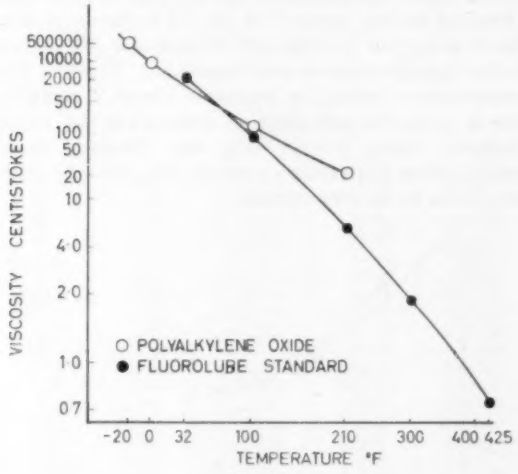

Fig 12

FLUOROLUBE STANDARD AND POLYALKYLENE OXIDE PLOTTED USING THE WALTHER–ASTM FORMULA

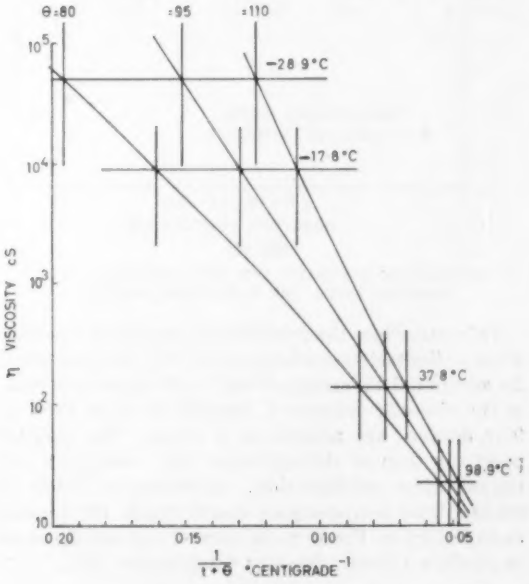

Fig 13

POLYALKYLENE OXIDE PLOTTED USING VALUES OF θ BETWEEN 80 AND 110. METHOD OF DETERMINING θ

corresponding to the experimentally determined viscosities at these temperatures, cutting the vertical lines. It is then possible to see which value of θ will

give a straight line. In the case shown the correct θ is 80; larger or smaller values of θ produce a relation curving away from the straight line.

These " fluorolube " results, taken from the ASME pressure–viscosity report,[11] are also plotted using the Walther–ASTM formula in Fig 12 and show a definite curve. Also a polyalkylene oxide, from the American Chemical Society paper,[11] of 141 VI is shown in this figure using the Walther–ASTM formula. It curves in the opposite sense to the fluorolube. Treating the experimental values, as explained above, a straight line is given for polyalkylene oxide with the Vogel formula, taking $\theta = 95$ (Fig 13). Plotting these results using Umstätter's formula (Fig 14), the lines are shown to be very curved.

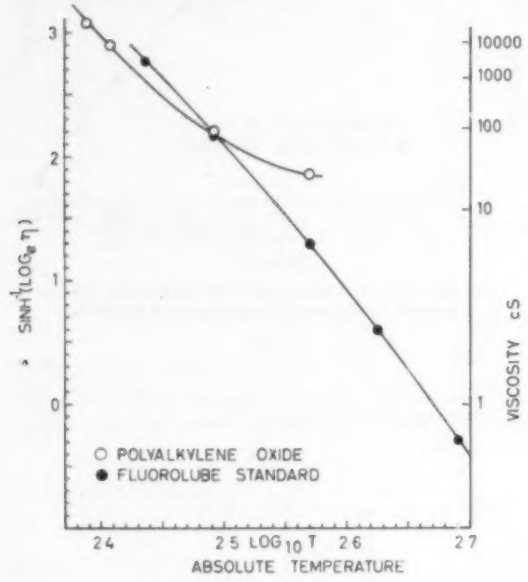

Fig 14

FLUOROLUBE STANDARD AND POLYALKYLENE OXIDE PLOTTED USING THE UMSTÄTTER FORMULA

This underlines the flexibility of the Vogel equation when no limitations are imposed on the three constants. An additional advantage of the Vogel equation is that, as the viscosity ordinate is logarithmic, only three or four decades are needed on a chart. The decimal point can then be shifted to suit the " thickness " of the oil under consideration. A number of sheets at standardized temperatures would enable the process as explained in Fig 11 to be carried out rapidly so as to produce a linear viscosity–temperature plot.

Use of Formulæ in Theoretical Calculations

In recent years increasing attention has been paid to the effect of viscosity variation on the load-carrying capacity of bearings. In all such work a convenient and simple viscosity temperature equation is required, the ones normally used being Reynolds',[1] Slotte's,[2] or Vogel's.[3] Reynolds' is valid only over a very limited temperature range, when the viscosity variation must also be small, and so this equation is not of much value.

Vogel's equation has been shown to be the most accurate, once the appropriate value of the constants has been determined. In general, θ varies (on the Centigrade scale) from 50° to 150° and b from 500° to 1500°. In calculations it is often most convenient to define a " viscosity " temperature scale starting at $-\theta$° Centigrade. Computation can then be done in terms of a non-dimensional temperature rise $\boldsymbol{T}$ defined as

$$\boldsymbol{T} = \frac{\text{Actual temperature °C} + \theta}{\text{Initial or ambient temperature} + \theta}$$

For example, if θ is 120 and, say, the ambient temperature is 40° C, then an actual temperature of 240° C will give a non-dimensional rise of

$$\boldsymbol{T} = \frac{240 + 120}{40 + 120} = 2\tfrac{1}{4}$$

Using this method the exact value of θ can often be left open, providing a wide enough range of $\boldsymbol{T}$ is studied.

In some calculations it is easier to use Slotte's equation, which avoids the exponential term. The values of the constants are best obtained by deriving first K, b, and θ for Vogel's law from three viscosities and then equating the subtangents. It is not possible to obtain them explicitly for Slotte's law. The subtangent of Vogel is $b/(t + \theta)^2$ and that of Slotte $m/(a + t)$. Thus as two given temperatures Slotte's m and a can be found in terms of Vogel's b and θ, which are already known. As Figs 1–4 show, Slotte does not fit as well as Vogel, so to minimize error the subtangents should be equated at points chosen with some care.

CONCLUSION

The two-constant formulæ due to Walther–ASTM and Umstätter show good correlation of results but are not reliable over extended ranges.

The most accurate of the formulæ for lubricants in present-day use is the three-constant formula due to Vogel, where θ is usually about 100 and b is about 1000 Centigrade units. This fits the observed viscosities of existing and experimental fluids over a wide range of temperatures. The formula is also simple mathematically, and each constant has a recognizable significance.

If computations are being made incorporating the variation of temperature in lubrication, by using a viscosity–temperature scale the zero of which is $-\theta$ the relative temperature rise can be used. In this way the values b and θ can be left open.

ACKNOWLEDGMENTS

The authors would like to thank Esso Research Ltd for giving permission to use their viscometers, which furnished the data in the Appendix, and particularly Dr R. Schnurmann for his help and advice. They would also like to thank The British Petroleum Co Ltd for a grant to one of them.

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APPENDIX

To measure the viscosities of the oils of −60 and 102 VI, the standard procedure[14] as carried out in most research laboratories was used. Glass-suspended level viscometers were first calibrated, a fixed volume of oil being timed by an electronic timer as it moved vertically through a capillary tube into an empty glass bulb. The results are tabulated below, together with the subtangent obtained by mathematical differentiation.

Temp, °C	Oil 1 −60 VI		Oil 2 102 VI	
	Viscosity, cS	$-\frac{1}{\eta}\frac{d\eta}{dt}$	Viscosity, cS	$-\frac{1}{\eta}\frac{d\eta}{dt}$
95	2·92	0·01922	13·31	0·02694
90	3·22	0·02051	15·22	0·02852
85	3·58	0·02189	17·54	0·03019
80	4·01	0·02353	20·46	0·03195
75	4·53	0·02517	24·12	0·03343
70	5·16	0·02654	28·67	0·03544
65	5·94	0·02895	34·40	0·03778
60	6·89	0·03116	41·86	0·04024
55	8·07	0·03356	51·56	0·04226
50	9·58	0·03710	64·09	0·04548
45	11·69	0·04107	81·74	0·04882
40	14·43	0·04341	105·3	0·05187
35	18·03	0·04742	137·7	0·05555
30	23·17	0·05101	183·8	0·06001
25	30·26	0·05665	251·9	0·06379
20	42·05	0·06380	351·1	0·06811
15	59·40	0·07008	502·5	0·07508
10	87·73	0·07663	759·2	0·08163
5	129·5	0·08726	1134	0·08726
0	211·9	0·10485	1765	0·09528
− 5	360·8	0·12262	2735	0·10575
−10	644	0·14275	4614	0·12294

SELECTIVE REDUCTION BY CALCIUM HEXAMMINE. PART III. APPLICATION TO AROMATICS IN OIL FRACTIONS *

By H. BOER † and P. M. DUINKER †

SUMMARY

Reduction by calcium hexammine has been applied in an investigation into the occurrence of diphenylalkanes in three gas-oil fractions.

In a Texan as well as in a Venezuelan gas-oil fraction some 12 per cent of the aromatics were shown to consist of diphenylalkanes. A check determination on an Indonesian gas-oil fraction, which, in view of its low final boiling point, was unlikely to contain a high percentage of diphenylalkanes, gave a correspondingly low result.

INTRODUCTION

In Part I of this series [1] it has been shown that under carefully adjusted reaction conditions calcium hexammine reduces condensed or conjugated polynuclear aromatic hydrocarbons to compounds containing only one isolated benzene ring. Thus naphthalenes are converted into tetralins and biphenyls into phenyl-*cyclo*hexanes, whereas diphenylalkanes are substantially unattacked.

This typical aspect of calcium hexammine reduction makes it possible, in principle, to determine the latter compounds in oil fractions. The present paper describes an application of this method to the analysis of three gas-oil fractions, namely,

(*a*) Indonesian, boiling range 280°–290° C
(*b*) Texan, boiling range 324°–330° C
(*c*) Venezuelan, boiling range 300°–325° C

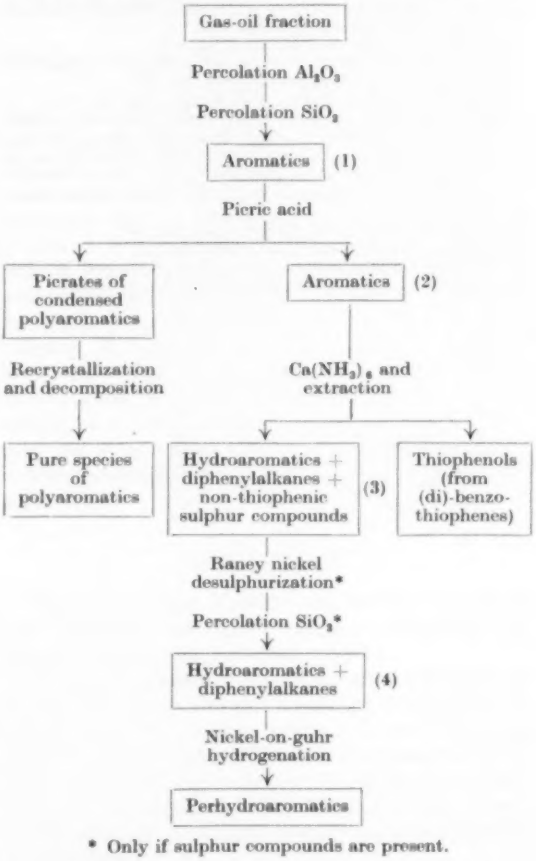
According to their boiling points, fractions (*b*) and (*c*) might contain simple diphenylalkanes, whereas the low boiling range of (*a*) precludes the presence of significant amounts of diphenylalkanes.

ANALYTICAL METHODS

The analyses of the gas oils are represented schematically below.

As shown in the scheme, the aromatics were first concentrated by chromatography. From this concentrate a few condensed polyaromatics could be isolated in the form of their picrates. The residual hydrocarbons were subjected to reduction by calcium hexammine.

The reaction product of the latter procedure consisted of hydroaromatics,‡ diphenylalkanes, and thiophenols (from benzothiophenes and dibenzothiophenes). The extraction and further analysis of the thiophenols are described elsewhere.[2,3] The mixture of hydroaromatics and diphenylalkanes remaining after extraction with alkali was analysed for the



* Only if sulphur compounds are present.

average number of benzene rings per molecule—from which the percentage of diphenylalkanes can be de-

* MS received 20 February 1961.
† Koninklijke/Shell-Laboratorium, Amsterdam.
Note: Part II appeared in *Rec. Trav. Chim.*, 1958, **77**, 935.

‡ In this paper the naphthenoaromatics resulting from the calcium hexammine hydrogenation of polyaromatics will be designated as hydroaromatics.

duced—by total hydrogenation and determination of the hydrogen content before and after. Corrections had to be applied for small amounts of *cyclo*-olefins produced by the calcium hexammine reduction (*cf* ref 1) and for slight cracking caused by the total hydrogenation. This modified "direct method" is described in the experimental part.

RESULTS

Table I gives a survey of the yields obtained after the successive treatments described in the analytical scheme.

TABLE I

Yields (% wt) of Concentrates after the Various Treatments of the Scheme

Gas-oil fraction	Concentrate			
	1	2	3	4
(*a*) Indonesian .	11·9	9·5	9·5	—
(*b*) Texan . .	9·4	6·9	5·7	—
(*c*) Venezuelan .	13·7	13·2	11·2	9·8

The elementary composition of the hydro- and perhydro-aromatic fractions is summarized in Table II.

TABLE II

Elementary Composition of Hydroaromatic and Related Perhydroaromatic Fractions

Oil fraction	Hydroaromatic fraction						Perhydroaromatic fraction			
	% C	% H	% S	% olefines	M	Emp. form	% C	% H	M	Emp. form
(*a*) Indonesian .	89·31	10·48	—	29·70	193	$C_{14\cdot26}H_{29\cdot06}$	86·47	13·47	196	$C_{14\cdot11}H_{36\cdot19}$
(*b*) Texan .	88·96	10·91	—	9·45	230	$C_{17\cdot01}H_{34\cdot89}$	86·49	13·50	225	$C_{16\cdot21}H_{30\cdot13}$
(*c*) Venezuelan .	88·57	10·76	0·24	14·10	221	$C_{16\cdot30}H_{33\cdot59}$, S 0·02	86·41	13·60	221	$C_{15\cdot90}H_{29\cdot93}$

The percentages of diphenylalkanes in the hydroaromatic fractions as found by the authors' method are presented in Table III.

TABLE III

Percentages of Diphenylalkanes in Hydroaromatic Fractions

Oil fraction	% diphenylalkanes on aromatics
(*a*) Indonesian	0·7
(*b*) Texan	11·8
(*c*) Venezuelan	12·5

In spite of the possibility of a rather considerable error, which is inherent in the determination of the average number of aromatic rings per molecule and which may be of the order of 4 per cent absolute in the present case, it is clear that fractions (*b*) and (*c*) contain considerable amounts of diphenylalkanes; the fact that only small amounts, if any, are present in the Indonesian gas-oil fraction was to be expected considering the low final boiling point.

1,3,7-Trimethylnaphthalene was isolated from the picrates from the Indonesian fraction and the Texan fraction yielded a pure methylphenanthrene, presumably 3-methylphenanthrene.

EXPERIMENTAL

Preparation of the Aromatic Concentrates

In each case 350 g of the gas-oil fraction was percolated through 3500 g of alumina (Peter Spence, Type H) and the aromatic fraction repercolated through silica (Davison 28–200 mesh) at an adsorbent/oil ratio of 20, so as to remove the last traces of saturates.

The Venezuelan hydroaromatic fraction, after desulphurization with Raney nickel, contained some 9 per cent of saturates, which were removed by percolation through silica at 0° C, in view of the olefins present.

Picric Acid Treatment of the Aromatic Concentrates

Equal weights of oil and picric acid dissolved in boiling ethanol were mixed. After cooling to room temperature the solid picrates were filtered and washed once with ethanol. In two cases recrystallization of the picrates, followed by their decomposition, yielded fairly pure aromatics. From the Indonesian fraction 1,3,7-trimethylnaphthalene was isolated, as could be deduced from the melting point of the picrate (141·5°–143° C, lit 144° C) and from the ultra-violet spectrum.[6] Texan gas oil yielded an alkylphenanthrene. The melting point of this compound and that of its picrate (63°–66° C and 143°–144° C, respectively) closely agreed with those recorded for 3-methylphenanthrene (65° C and 141° C, respectively). Unfortunately, the differences in the ultra-violet spectra of the five methylphenanthrenes were too small to permit a positive identification as 3-methylphenanthrene.

Hydrogenation with Calcium Hexammine

The calcium hexammine reagent was prepared by introducing ammonia gas into an ethereal suspension of calcium, as described in Part I.[1] The molar ratio of calcium to oil was 3·5. The reaction temperature was 0° C; the reaction time 1½ hr. After the reaction

calcium amide and unconverted $Ca(NH_3)_6$ were filtered off in a nitrogen atmosphere and the filter cake was washed with dry ether.

Completeness of the hydrogenation of the poly-aromatics was checked by the ultra-violet spectra of the filtrates, after evaporation of the ether. Only with the Venezuelan sample, which still contained some 5 per cent of diaromatics, was an additional hydrogenation, employing a small amount of calcium, necessary.

Desulphurization with Raney Nickel

To an ethanolic solution containing the hydro-aromatics and non-thiophenic sulphur compounds, freshly prepared Raney nickel, stored under ethanol (10 g per g of sulphur compounds) was added. After refluxing for 5 hours, the Raney nickel was filtered off and extracted with ethanol in a Soxhlet apparatus. This procedure was repeated once.

Total Hydrogenation of Hydroaromatics

The hydroaromatic fractions were pre-hydrogenated with a nickel-on-guhr catalyst (cat/oil = 1) for 5 hours at a maximum hydrogen pressure of 250 kg/cm² and a reaction temperature of 300° C. After filtering off the catalyst and extraction in a Soxhlet apparatus the whole procedure was repeated for 50 hours with fresh catalyst.

The last traces of aromatics (0·4–1 per cent) were removed by percolation through silica.

Ring Analysis by a Modified "Direct Method"

Aromatic ring analysis in the hydrocarbon fractions was performed by total hydrogenation and determination of the increase in hydrogen content (direct method). For the application of this method the molecular weight must be known.[4]

An oil fraction containing only monoaromatics and having the formula C_cH_h will, after total catalytic hydrogenation, have the formula $C_cH_{h'}$, where $h' - h = 6{\cdot}0$. If this fraction also contains diphenylalkanes, $h' - h > 6$ and the percentage of diphenylalkanes is:

$$\frac{h' - h - 6}{6} \cdot 100 \text{ per cent} \quad . \quad . \quad . \quad (1)$$

This formula cannot, however, be applied to poly-aromatics hydrogenated with calcium hexammine, as these fractions often contain cyclic olefins.[1] Removal of such olefins by an additional mild catalytic hydrogenation in the case of oil fractions sometimes gives rise to difficulties. Therefore it is easier to correct equation (1) by an exact ozonometric determination of the amount of olefins.[5]

When a percentage of olefins is present the number of carbon atoms in aromatic structure is $h' - h - 0{\cdot}02a$ and the percentage of diphenylalkanes is given by:

$$\frac{h' - h - 0{\cdot}02a - 6}{6} \cdot 100 \text{ per cent} \quad . \quad . \quad (2)$$

Another correction has to be made for slight cracking during total hydrogenation. This may be reflected in a decrease of the mean number of carbon atoms ($C_cH_{h'}$ instead of $C_cH_{h'}$). Assuming that the decrease is caused by splitting off CH_2-groups, one may transform equation (2) into:

$$\% \text{ diphenylalkanes} = \frac{(h' - h) + 2(c - c') - 0{\cdot}02a - 6}{6} \cdot 100 \quad . \quad (3)$$

Application of this formula to the data in Table II yielded the percentages given in Table III.

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SELECTIVE REDUCTION BY CALCIUM HEXAMMINE. PART IV[1]. APPLICATION TO SULPHUR COMPOUNDS IN A GAS OIL *

By J. KNOTNERUS,† P. M. DUINKER,† and J. VAN SCHOOTEN†

SUMMARY

Reduction by calcium hexammine has been applied to aromatic fractions of a Venezuelan heavy gas oil containing sulphur compounds. In this reaction benzothiophenes were converted into thiophenols, which were separated from the hydrocarbons and desulphurized with the aid of Raney nickel. The alkylbenzenes finally obtained were analysed by ozonolysis.

It appeared that the benzothiophenes in this gas oil are substituted by many (3·6–4·9) short side chains, a remarkable feature being the frequent occupation of the 2-position.

Biphenyl, originating from dibenzothiophene, was also isolated from the desulphurized products.

The saturated sulphur compounds also occurring in the aromatic fractions of the gas oil did not react with calcium hexammine, but could be desulphurized with Raney nickel. They are of a naphthenic nature, the sulphur atom forming part of a saturated ring.

INTRODUCTION

Of the sulphur compounds which occur in gas-oil and lubricating-oil fractions[2] only the saturated ones can be separated from the aromatic hydrocarbons by the conventional extraction and chromatographic methods owing to their Lewis basicity. However, from the investigation described in Part II,[3] it is known that the non-extractable sulphur compounds, such as benzo- and dibenzothiophenes, are readily reduced by calcium hexammine to form thiophenols which can be separated as such. Further examination of these compounds may then provide information on the structure of the original sulphur compounds.

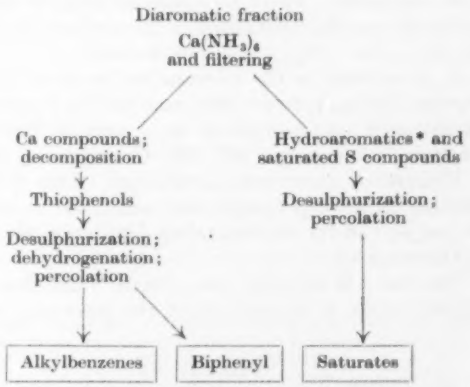
The application of the reduction method to two Venezuelan oil distillate fractions is described in this paper.

METHODS AND RESULTS

Two different routes (A and B) have been followed in investigating the two distillate fractions.

A. The diaromatic part of a fraction, boiling range 300°–325° C, obtained by chromatographic methods and consequently free from thiols, was chosen as the starting material for the first series of experiments carried out according to the following scheme.

The aromatic fraction was treated with calcium hexammine and filtered. The thiophenols formed remained bound to the solid calcium compounds, and could thus be separated. After the thiophenols had been desulphurized with the aid of Raney nickel and small amounts of hydroaromatics formed had been dehydrogenated (under the influence of a Pt/Al_2O_3 catalyst in the liquid phase at 200°–220° C, while a stream of nitrogen was passed through the reaction mixture) an aromatic hydrocarbon fraction was obtained, 30 per cent of which consisted of biphenyl and 70 per cent of alkylbenzenes. These two types of compound were separated from each other by percolation through Al_2O_3.



* The term "hydroaromatics" here denotes compounds which have been formed from the diaromatics by partial reduction and which can be easily re-converted into the latter.

The biphenyl fraction, which according to an ultra-violet analysis was 96 per cent pure and had a melting point of 66·9°–68·7° C, must have originated from dibenzothiophene. From the results of the present work it appeared that the amount of dibenzothiophene present in the original aromatic fraction was at least 4 per cent.‡

The alkylbenzenes originated from benzothiophenes; ultra-violet analysis indicated that they constituted a purely monoaromatic type concentrate. According to elemental analysis and a molecular-weight determination, the average overall formula was $C_{14.4}H_{22.5}$. Ozonolysis[4] of these alkylbenzenes produced quantita-

* MS received 20 February 1961.
† Koninklijke/Shell-Laboratorium, Amsterdam.

‡ This corresponds well with the content of dibenzothiophene (at least 3 per cent) found previously by ultra-violet analysis.

tive information concerning the degree of substitution and the nature of the substituents, shown in Table I.

TABLE I

Ozonolysis of Monoaromatic Substances Formed from the Benzothiophenes present in a Venezuelan Mineral Oil Distillate, Boiling Range 300°–325° C

	Substituents					
	CH_3	C_2H_5	i-C_3H_7	n-C_3H_7	sec-C_4H_9	n-C_4H_9
Side chains, "mol% "	58·5	13·7	4·2	12·1	4·5	5·9
Number of side chains per molecule	2·75	0·65	0·2	0·6	0·2	0·3

The oil which, after the reaction with $Ca(NH_3)_6$, was recovered from the filtrate of the calcium compounds, contained saturated sulphur compounds. After desulphurization and percolation through silica gel, a saturated fraction was obtained, the yield of which corresponded with the amount of sulphur compounds which had not reacted with $Ca(NH_3)_6$. These saturated hydrocarbons could not be dehydrogenated to form aromatics. From an elemental analysis and a molecular-weight determination an average formula $C_{16\cdot3}H_{31\cdot7}$, *i.e.* C_nH_{2n-1}, could be deduced.

B. In addition to the investigation on the aromatic fraction boiling between 300° and 325° C, a series of experiments was performed on a narrow distillate fraction, boiling range 292°–296° C, originating from a Venezuelan diaromatic concentrate. This narrow fraction of the type concentrate amounted to about 10 per cent of the corresponding distillation fraction of the crude oil.

The route B followed here differed from that described under A, in sequence of the successive steps

TABLE II

Separation of Venezuelan Diaromatic Fraction with the Aid of Basic Al_2O_3

Fraction No.	Yield, % wt	% S	n_D^{25}	Mol weight	Eluted with
1	80·2	4·5	1·5883	188	Pentane + benzene
2	10·4	6·0	1·5790		Pentane + benzene
3	6·2	11·3	1·5336		Ether
4	2·5	14·1	1·5732		Ethanol
Original diaromatic fraction		5·5	1·5849	200	

and in method of isolation of the thiophenols. The aromatic fraction was first percolated through "basic" aluminium oxide* in order to obtain a diaromatic fraction free from saturated sulphur compounds.

Table II gives some data on the fractions thus obtained.

It may be assumed that the fractions 1 and 2 contained all the benzothiophenes present. 10–15 per cent of the sulphur compounds in fraction 2 were aliphatic, whereas fraction 3 contained almost exclusively aliphatic sulphur compounds (these compounds react with iodine to form complexes giving a characteristic ultra-violet spectrum[5]). The nature of the sulphur compounds of the fourth fraction is not known.

From these figures it can easily be calculated that at least 76 per cent of the sulphur compounds present in the original diaromatic type concentrate fraction are benzothiophenes. At least 12 per cent of the sulphur compounds of this fraction could be shown to be aliphatic.[5]

Thus the amounts of benzothiophenes and saturated sulphur compounds in this diaromatic fraction can be roughly estimated at 25 per cent and 4 per cent respectively (supposing a molecular weight of about 190). As the diaromatic fraction is about 10 per cent of the corresponding crude oil fraction, it follows that this narrow gas-oil fraction contains at least 2·5 per cent and 0·4 per cent of the two different types of sulphur compounds.

TABLE III

Ozonolysis of Monoaromatics Formed from Benzothiophenes Present in a Venezuelan Diaromatic Type Concentrate, Boiling Range 292°–296° C

	Substituents					
	CH_3	C_2H_5	i-C_3H_7	n-C_3H_7	sec-C_4H_9	n-C_4H_9
Alkylbenzenes from thiophenols extracted with aqueous alkali, mol %	60	18	0	8	9	5
Alkylbenzenes from thiophenols extracted with alcoholic alkali, mol %	59	14	3	11·5	7	5
Average number of side chains per molecule	2·1	0·55	0·05	0·35	0·3	0·15

Fraction 1 (Table II) was treated with calcium hexammine. For a complete conversion of the benzothiophenes a reaction period of 4 hours at 0° C appeared to be necessary, whereas with model compounds 1–1·5 hours was sufficient.[3] The reaction product was extracted first with an aqueous caustic alkali solution and then with dilute (50 per cent v) methylalcoholic alkali.† The two fractions of thiophenols obtained were desulphurized with the aid of Raney nickel. The sulphur-free hydrocarbons finally obtained appeared to consist

* Woelm, Germany.

† The extraction of the thiophenols formed was not quite complete, owing to the easy oxidation of these compounds to disulphides and the unfavourable distribution coefficient of the mercaptides in this molecular-weight range over the hydrocarbon and the aqueous layer. Reaction route A is therefore preferred.

almost exclusively of alkylbenzenes (ultra-violet analysis). According to a mass-spectrometric analysis they contained mainly C_{12}-aromatics, the average number of C-atoms per molecule being 12·2 for one fraction and 12·35 for the other.

Ozonolysis of the hydrocarbon fractions produced the results shown in Table III.

DISCUSSION

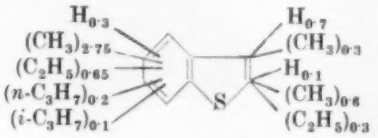
A further interpretation of the results shown by Tables I and III is possible when it is assumed that all butyl groups originate from the thiophene ring, in such a way that two out of the four butyl C-atoms had belonged to the ring itself, *e.g.*:

This assumption is supported by the fact that *iso*-butyl and tertiary butyl groups, which could not possibly have originated from the thiophene ring, actually do not occur.

The propyl groups can have originated from the thiophene ring as well, with the restriction, however, that for the alkylbenzenes obtained by the methods of route A the degree of substitution is so high that part of the propyl groups must have been substituted in the benzene ring.

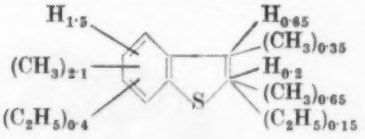
When the alkylbenzenes of the two oil fractions are compared, slight differences are noted, apparently depending on their molecular weight. To the original benzothiophenes the following average formulæ may be assigned:

(*a*) Benzothiophenes from the oil fraction with boiling range 300°–325° C (route A):



This overall formula $C_{14·45}H_{18·9}S$, molecular weight calculated at 224, gives an idea of the degree of substitution and of the nature of the substituents. The degree of substitution appears to be high (value found: 4·9, maximum value possible: 6·0), whereas the substituents themselves are small.

(*b*) Benzothiophenes from the oil fraction with boiling range 292°–296° C (route B):



Overall formula $C_{12·2}H_{14·4}S$; molecular weight calculated at 193. A value of 188 was found for the molecular weight of the starting fraction, eluted from basic Al_2O_3.

Apparently, a lower molecular weight corresponds with both a lower degree of substitution and a lower C_2H_5/CH_3 ratio (0·18 as against 0·26 in the former case). For both groups of benzothiophenes the degree of substitution appears to be considerably higher at the 2-position than at the 3-position.

Although the benzothiophene fraction could in principle contain a large number of individual compounds, gas–liquid chromatography of the first alkylbenzene fraction mentioned in Table III revealed a diagram less complicated than expected (Fig 1).

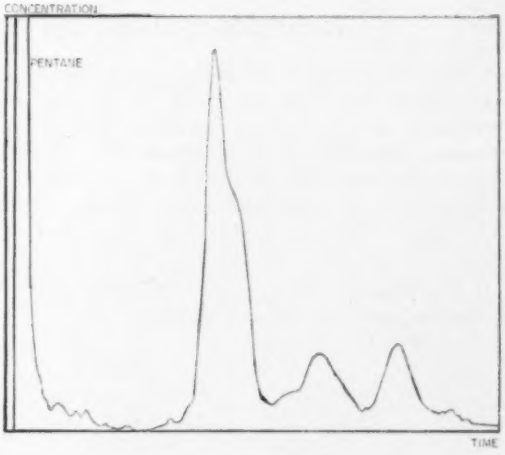
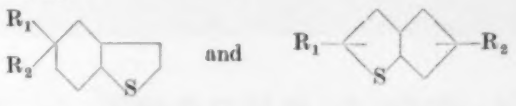


FIG 1

GLC DIAGRAM OF ALKYLBENZENES DERIVED FROM THE BENZOTHIOPHENES OCCURRING IN A VENEZUELAN GAS OIL FRACTION, BP 292°–296° C

According to its average formula and properties, the hydrocarbon fraction originating from the saturated sulphur compounds (route A) does not consist of naphthenes of the perhydroaromatic type; the naphthenic compounds consequently contain six-membered rings with a quaternary C-atom or five-membered rings. In the original sulphur compounds the S-atom must have formed part of the ring structure; there can be no question of aliphatic sulphides, because in that case the molecular weight of the desulphurized product would have been lower. Possible types of structures are, *e.g.*



It should be stated here that this molecular weight (228) still equalled that of the original aromatic fraction. Therefore the saturated sulphur compounds

contained per molecule about 2 C-atoms more than the benzothiophenes from the same distillate fraction. A similar difference was found between the saturated and aromatic hydrocarbons in a given fraction.

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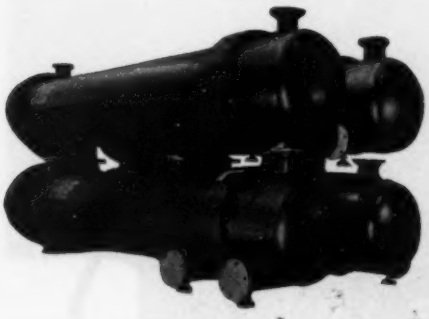

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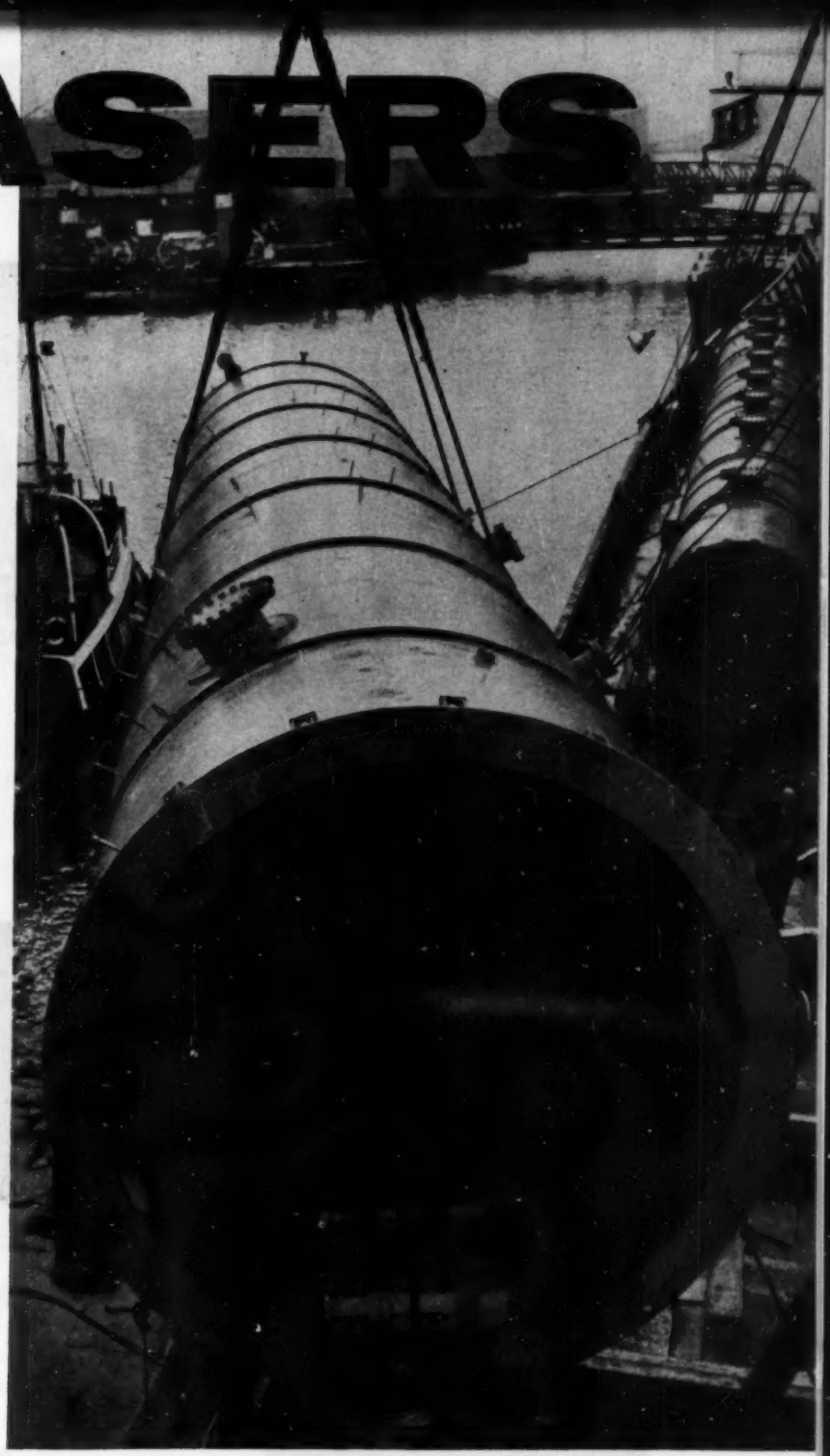

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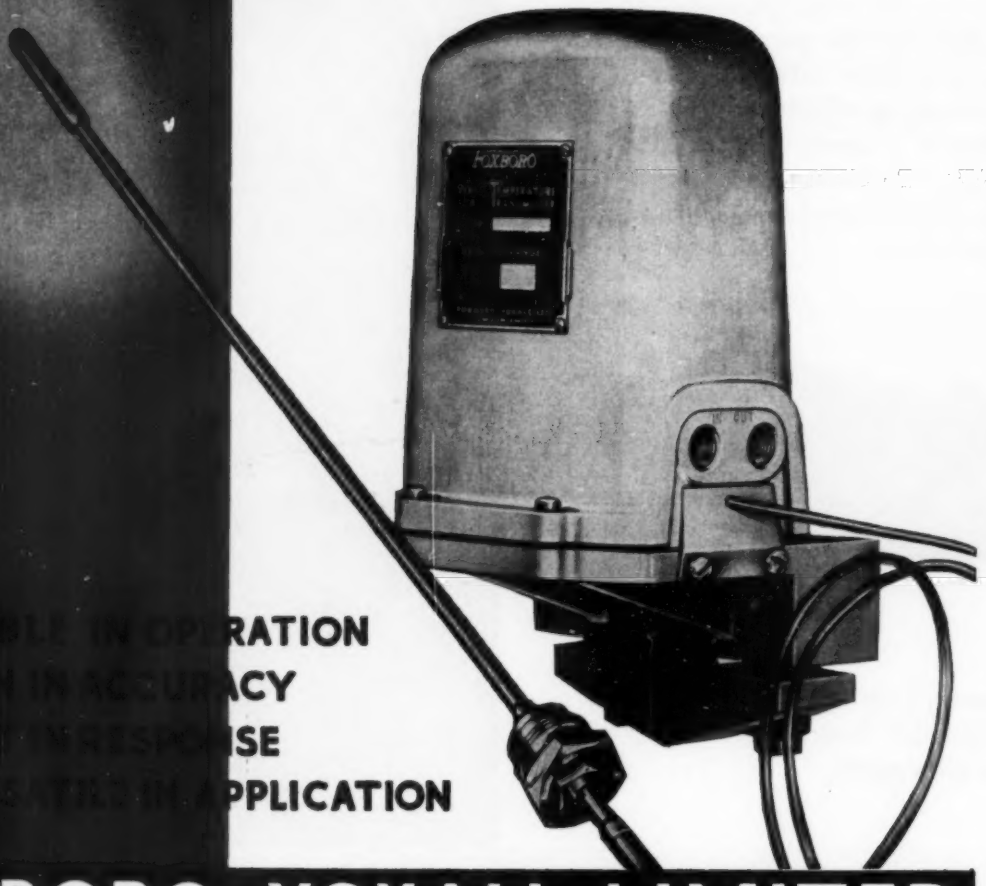

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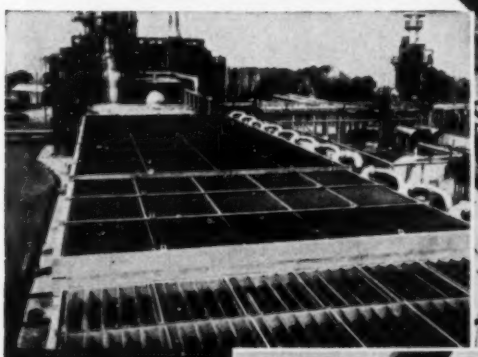

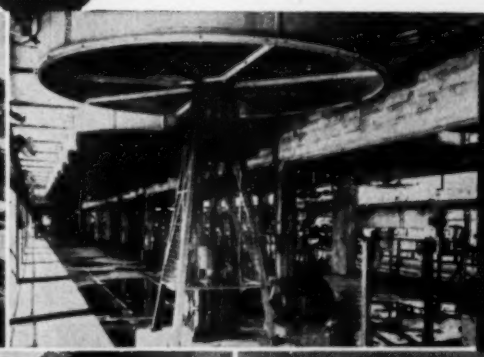

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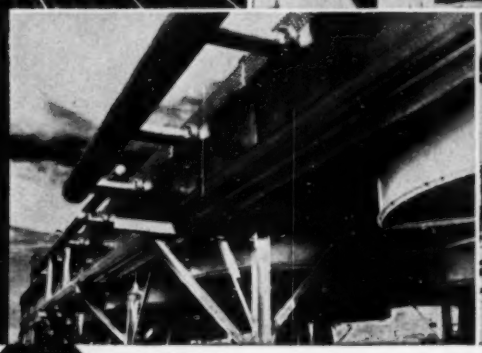

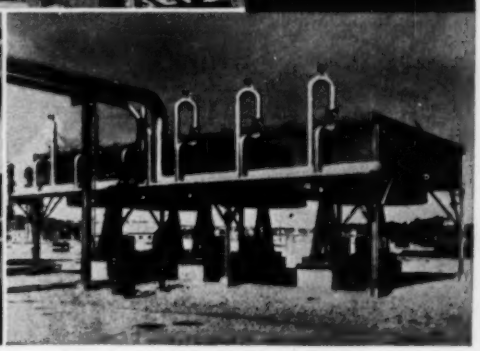

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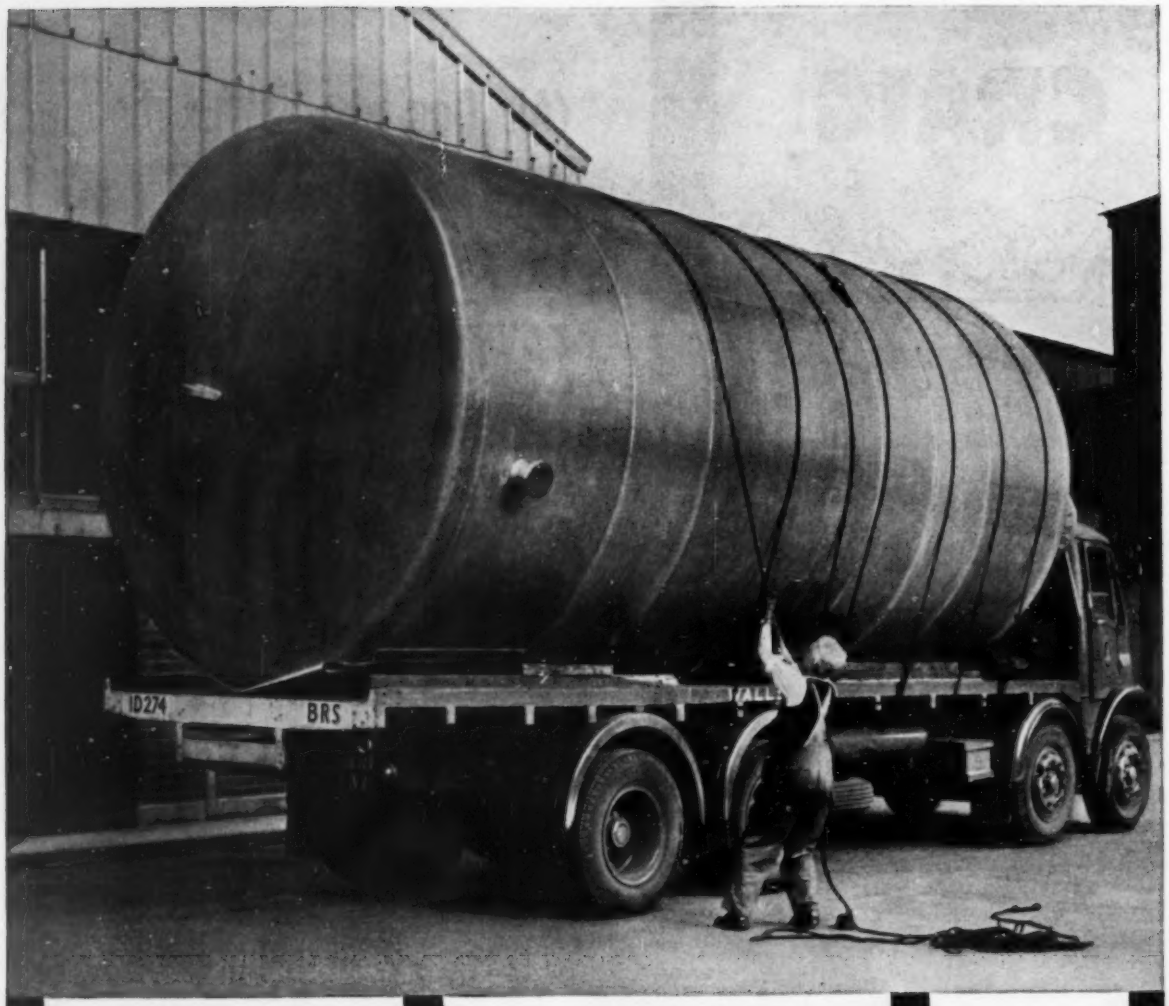

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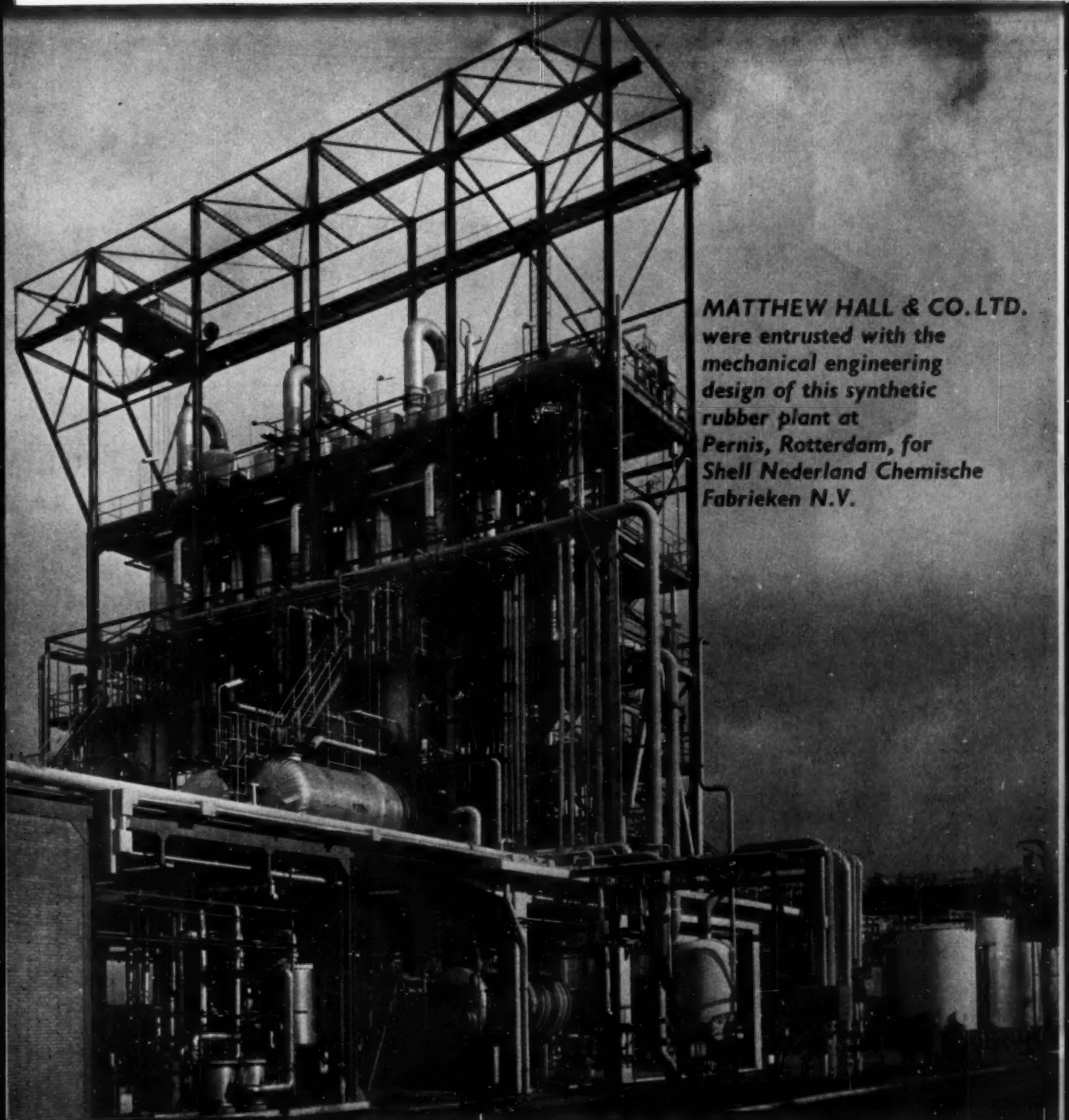

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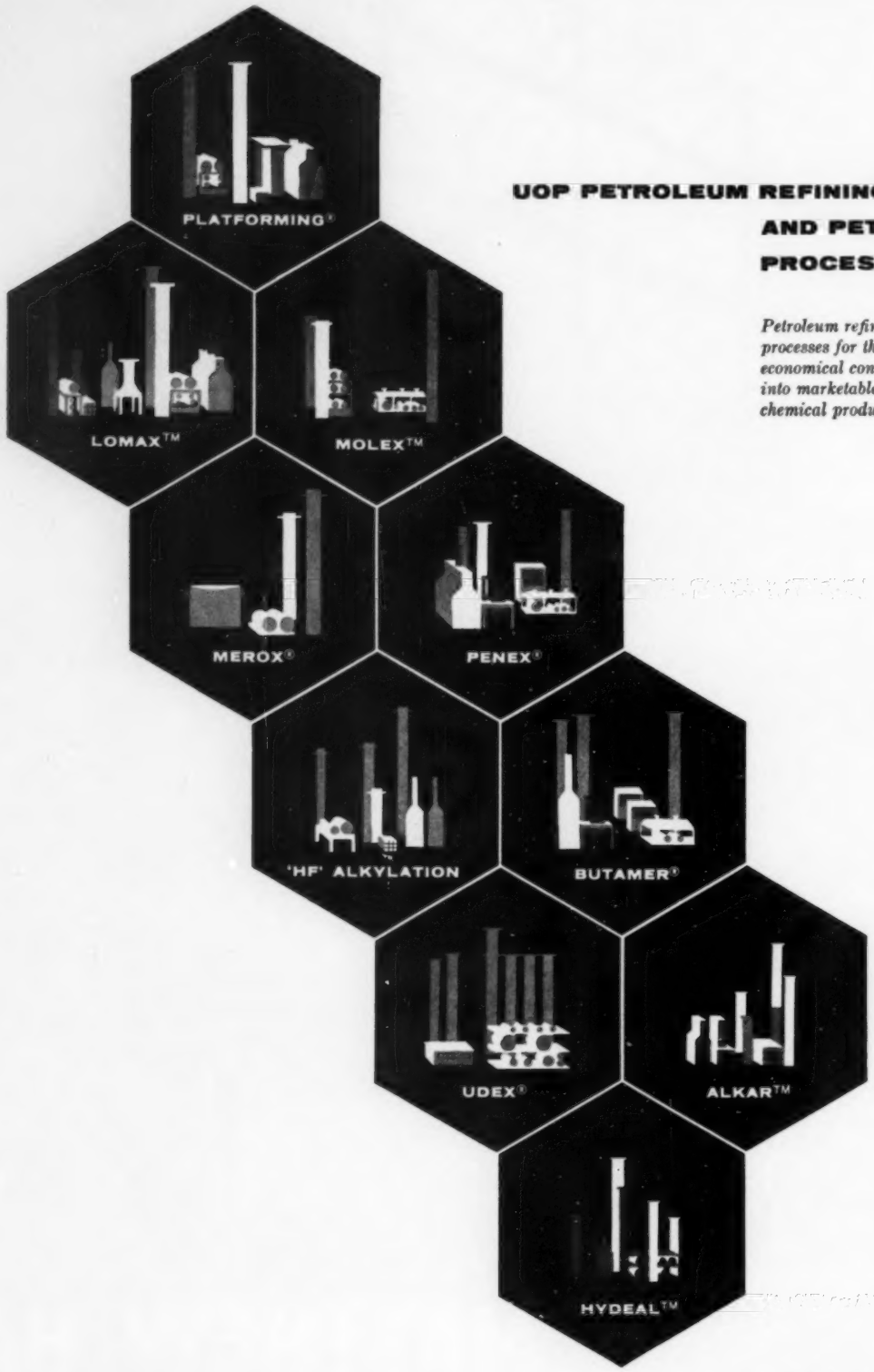

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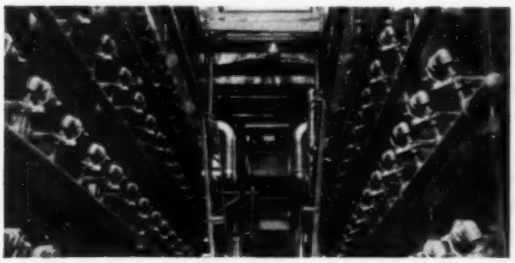

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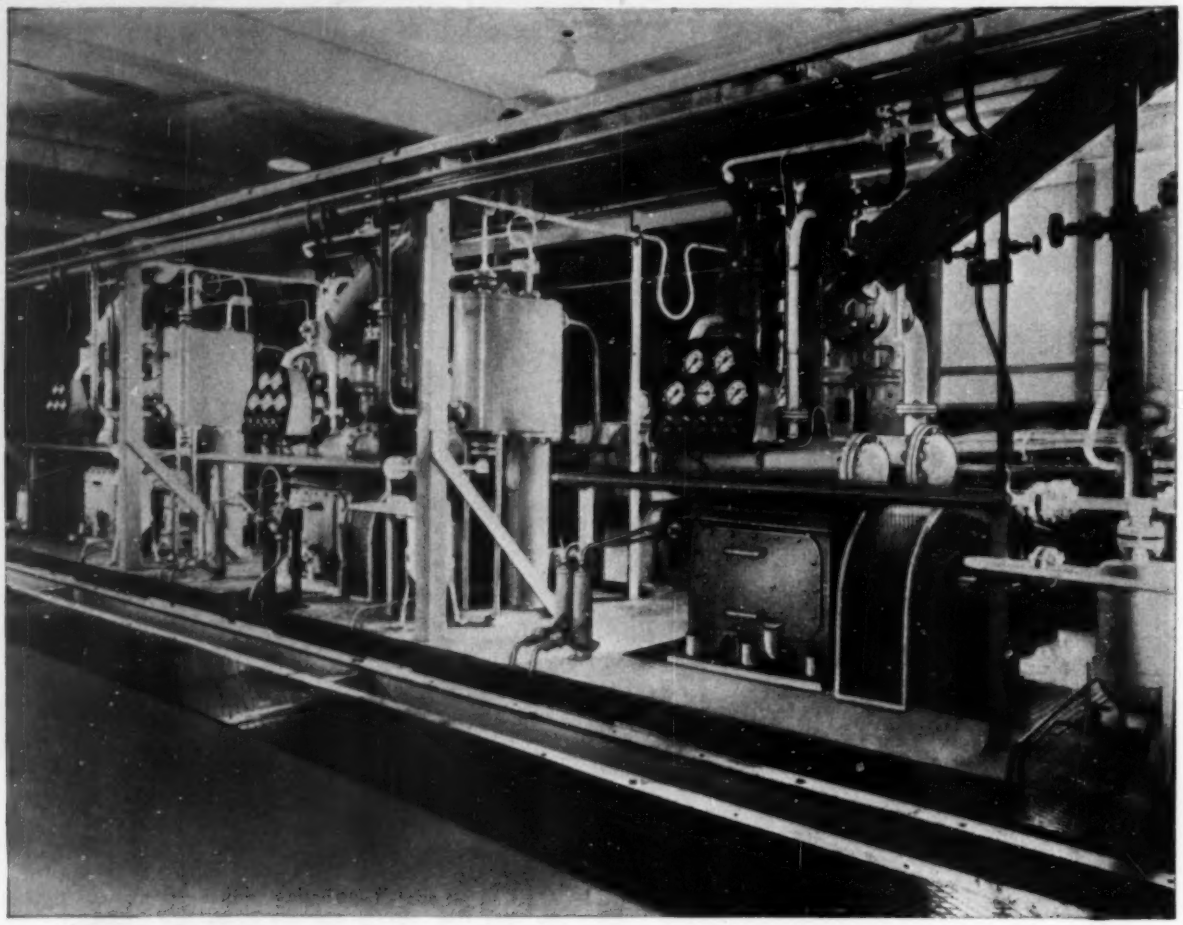

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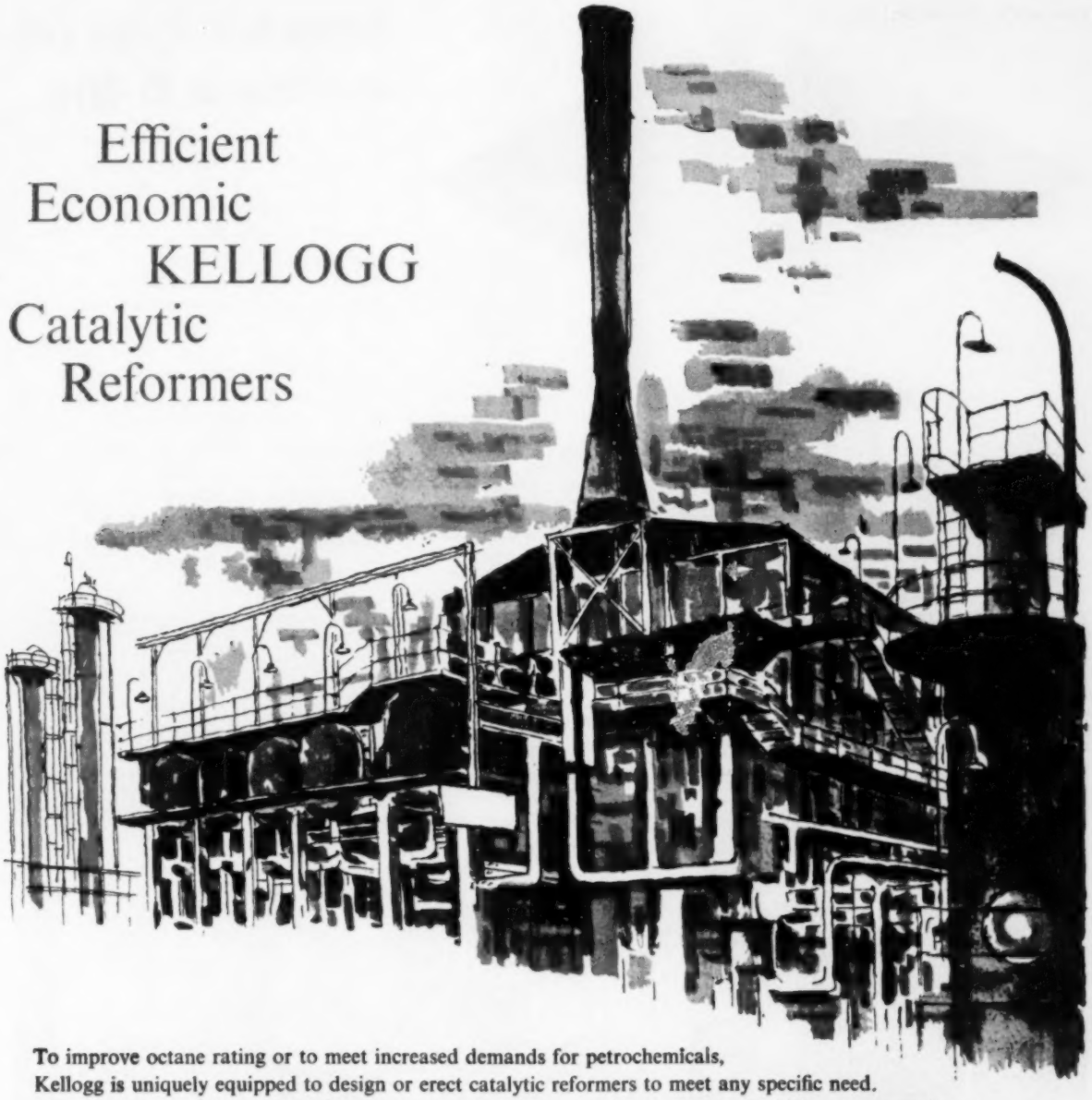

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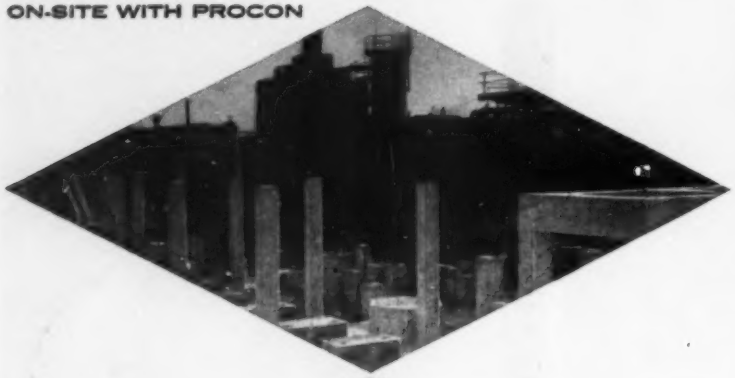

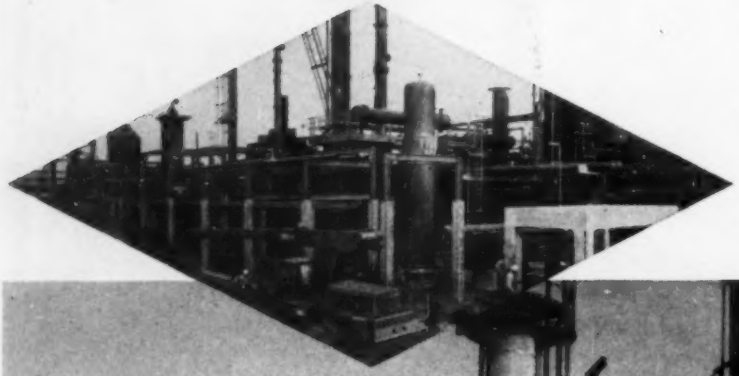

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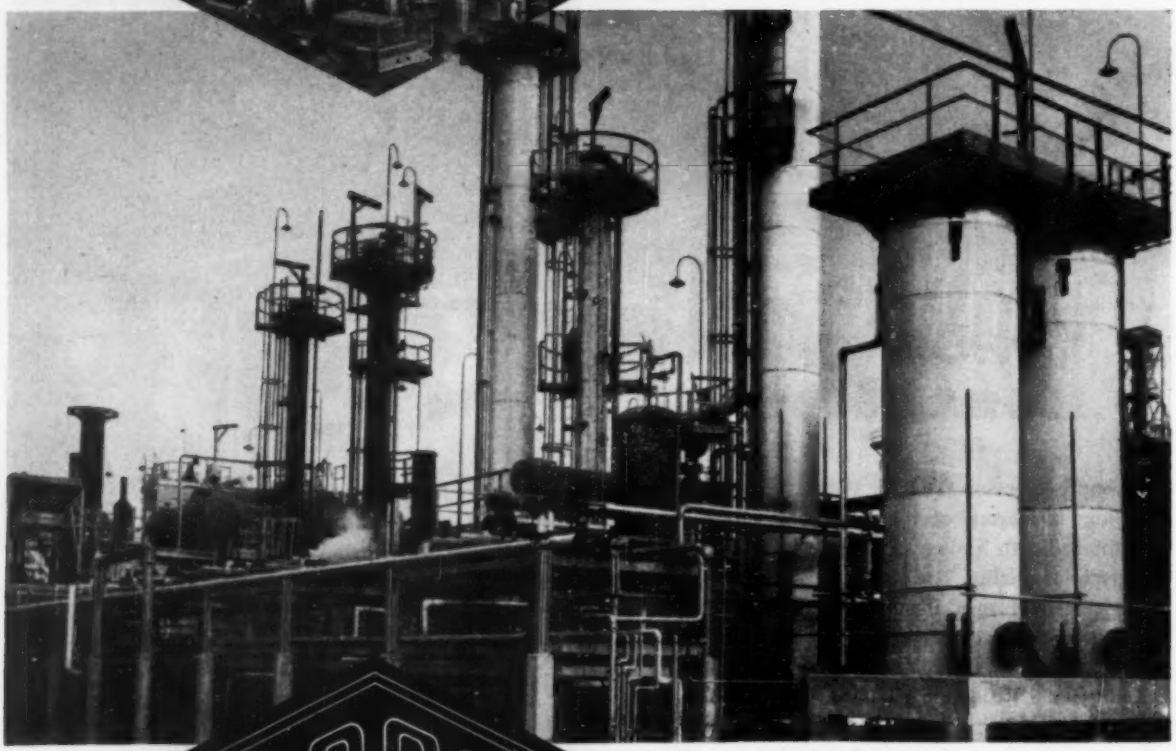

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